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ÉTUDE DE LA PHÉNYL-2 OXINE ET DE SES CHÉLATES

III. PRÉPARATION ET PROPRIÉTÉS DES PHÉNYL-2 OXINATES

par

GEORGES BOCQUET ET RENÉ A. PÂRIS

Laboratoire de Chimie Minérale de la Faculté des Sciences de Lyon (France)

Dans deux précédents articles de cette Revue^{1,2}, nous avons indiqué les principales caractéristiques de la phényl-2 oxine (phényl-2 hydroxy-8 quinoléine). Mais une propriété essentielle de cette phényl-2 oxine, comme de l'oxine dont elle dérive, est de pouvoir former avec les ions métalliques des "complexes internes de chélation" (plus brièvement, des "chélates"), dans lesquels la coordinence de l'ion central est souvent complétée par l'addition de molécules d'eau (par exemple).

On sait que dans la formation de tels composés, il faut fréquemment faire intervenir la notion d'empêchement stérique. En particulier, pour les dérivés α -substitués de l'oxine, certains chélates sont exclus, les autres voient leur stabilité modifiée ainsi que le nombre de leurs molécules d'eau de cristallisation.

D'où l'intérêt d'une étude des phényl-2 oxinates qui permette la comparaison des résultats avec ceux précédemment publiés pour les oxinates^{3,4} et les méthyl-2 oxinates^{3,5}.

I. ÉTUDE POTENTIOMÉTRIQUE DE LA PRÉCIPITATION

Une telle étude permet d'atteindre les produits de solubilité ou les constantes de stabilité des chélates. Mais pour effectuer une comparaison valable des différents réactifs, il eut fallu pouvoir les étudier dans les mêmes conditions. Or, nous savons¹ que la phényl-2 oxine est beaucoup moins soluble dans l'eau que l'oxine ou la méthyl-2 oxine, et qu'il est nécessaire d'opérer, par exemple, en milieu hydro-alcoolique; il en résulte évidemment un certain décalage des valeurs observées par rapport au milieu aqueux.

Nous avons cependant établi⁶ des courbes de neutralisation, qui nous ont au moins permis de situer les zones de formation des chélates.

Ces courbes, dont trois exemplaires sont reproduits sur la Fig. 1, ont été obtenues dans les mêmes conditions (milieu hydroalcoolique 45° G.L.) que la courbe de neutralisation de la phényl-2 oxine précédemment décrite²: on ajoutait simplement au milieu la quantité théorique d'ions métalliques.

Sur ces courbes, la formation de chélate se traduit par l'apparition d'un "palier", que nous repérons par le point d'inflexion M. On notera, tout particulièrement dans le cas du phényloxinate de zinc (courbe 1), qu'il faut faire la distinction entre la

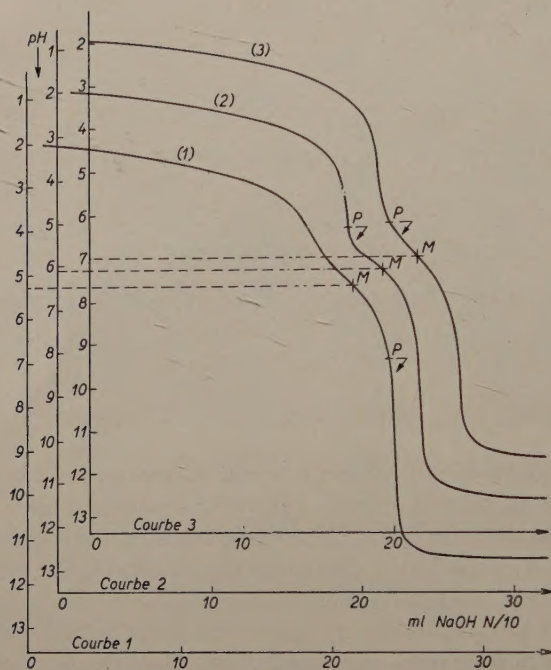


Fig. 1. Potentiométrie des phényloxinates.
Courbe 1: Zn; courbe 2: Cd; courbe 3: Ni.

formation d'un chélate et sa précipitation. Nous donnons dans le Tableau I, pour une série de cations bivalents, les pH de début de précipitation (points P) et les „pH de formation” (points M).

TABLEAU I

Cation	pH de début de précipitation	pH de formation
Zn ⁺²	6.90	5.30
Cd ⁺²	5.20	6.15
Ni ⁺²	6.30	7.05
Co ⁺²	6.30	6.95
Hg ⁺²	6.45	7.30
Mn ⁺²	7.55	8.30
Pb ⁺²	4.05	6.00
Cu ⁺²	2.75	<4

Des courbes plus complexes ont été obtenues⁶ avec Fe⁺², Fe⁺³, Tl⁺³, MoO₄⁻², WO₄⁻², VO₃⁻. Parmi les précipités correspondants, seuls ceux de Tl, Mo et Fe^{II} se sont révélés à l'analyse thermogravimétrique être des produits définis.

Enfin, ni Al⁺³, ni Mg⁺², ni Cr⁺³ ne donnent lieu à la formation d'un chélate, alors que l'on connaît les méthyl-2 oxinates de Mg et Cr et les oxinates de Al, Mg et Cr. Un certain accroissement de sélectivité a donc bien été obtenu par l'introduction du groupement phényle à la place du groupement méthyle, en α de l'atome d'azote de l'oxine.

II. ANALYSE THERMOGRAVIMÉTRIQUE DES PHÉNYL-2 OXINATES

Préparation des phényl-2 oxinates

Le mode opératoire utilisé par BORREL ET PÂRIS^{4,5} pour les oxinates et méthyl-2 oxinates ne s'applique pas à la phényl-2 oxine: il faut en effet opérer en milieu hydroalcoolique. Or, il arrive que si l'on ajoute assez d'alcool (45 à 50%) pour empêcher toute coprécipitation du réactif, il n'est, dans certains cas (Zn, Co), plus possible d'obtenir la précipitation du chélate. Et, d'autre part, de telles teneurs en alcool gênent la fixation des molécules d'eau sur les chélates; on ne peut pas rassembler le précipité à chaud, sous peine de le déshydrater plus ou moins, voire même le dissoudre selon la quantité d'alcool présente.

A la suite de divers essais, nous avons adopté le mode opératoire suivant:

A des volumes égaux de la solution hydroalcoolique (45%) acide (N/5) du réactif (M/20) et de la solution aqueuse de l'ion métallique (M/40 pour un cation bivalent), on ajoute les quantités d'alcool et d'éther nécessaires pour que la proportion finale soit de 30% en alcool et 15% en éther. On provoque la précipitation en neutralisant progressivement, et sous agitation, par la soude normale. Le précipité est lavé deux fois par décantation avec un mélange eau-alcool 30% — éther 15%, recueilli sur creuset filtrant Pyrex no. 3 ou 4, et enfin, séché une nuit par aspiration d'un courant d'air à travers le filtre.

Nous avons cherché à obtenir des chélates possédant leur nombre maximum de molécules d'eau. Mais il n'est pas exclu qu'un autre mode opératoire puisse donner des résultats différents, comme nous avons pu l'observer pour l'oxinate de plomb (voir plus loin, Tableau III).

Analyse thermogravimétrique: mode opératoire

L'appareil utilisé était la thermobalance de CHEVENARD, avec, bien entendu, le même régime thermique que celui adopté par BORREL ET PÂRIS pour leur étude des oxinates⁴ et des méthyl-2 oxinates⁵: montée linéaire d'environ 3 degrés par minute jusqu'à 700° C et maintien 2 heures à cette température. On ne doit pas, en effet, perdre de vue, pour l'interprétation des résultats d'analyses thermogravimétriques de sources diverses, que ceux-ci dépendent non seulement du mode opératoire suivi pour la préparation du produit étudié, mais aussi du régime thermique utilisé.

La sensibilité de l'appareil était telle que 200 mg correspondaient à 154-155 mm sur le papier photographique.

Le poids initial de précipité analysé était de 300 à 400 mg. La perte de poids totale était connue en pesant le creuset avant et après l'opération; les pertes partielles étaient mesurées sur les courbes.

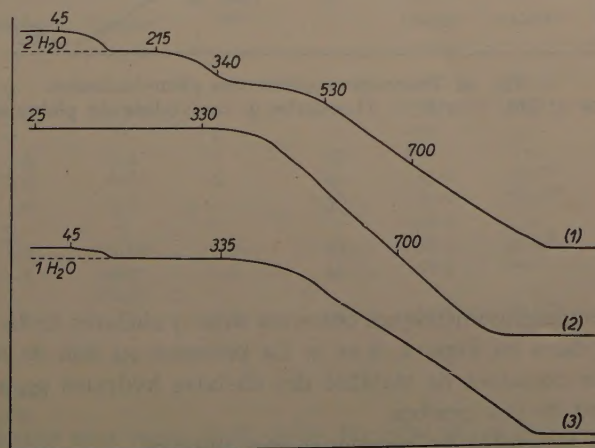


Fig. 2. Thermogravimétrie des phényloxinates.
Courbe 1: Cu; courbe 2: Zn; courbe 3: Cd.

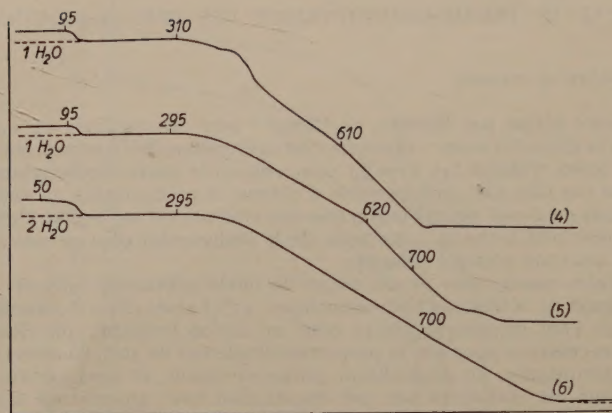


Fig. 3. Thermogravimétrie des phényloxinates.
Courbe 4: Ni; courbe 5: Co; courbe 6: Pb.

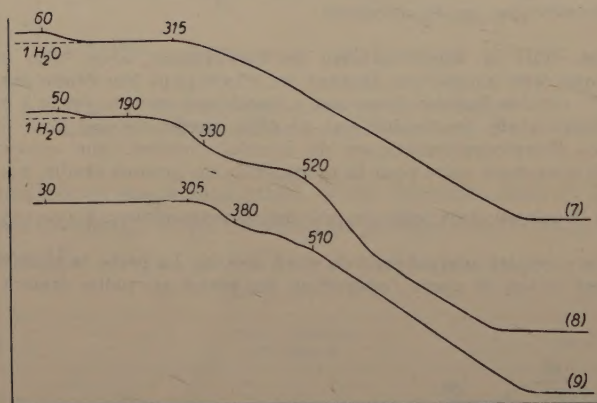


Fig. 4. Thermogravimétrie des phényloxinates.
Courbe 7: Mn; courbe 8: Tl; courbe 9: molybdate de phényloxine.

Résultats

Les courbes thermogravimétriques obtenues avec 9 chélates de la phényl-2 oxine sont reproduites dans les Figs. 2, 3 et 4. La présence ou non de molécules d'eau d'hydratation, les domaines de stabilité des chélates hydratés ou anhydres se déduisent facilement de ces courbes.

Le Tableau II rassemble les renseignements obtenus.

Θ_1 désigne la température de début de déshydratation d'un chélate hydraté, Θ_2 la température de début de pyrolyse du chélate anhydre.

TABLEAU II

Phényl-oxinates	Couleur	Températures		Perte de poids (%) totale		Perte de poids (%) par déshydratation	
		Θ_1 °C	Θ_2 °C	Expérimentale*	Théorique	Expérimentale	Théorique
Cu(PhOx) ₂ 2H ₂ O	Noir verdâtre	45	215	84.7 85.3 85.3	85.3 " "	6.75* 7.9 7.5	6.67 " "
Zn(PhOx) ₂ anh.	Jaune vif	—	330	83.5 84.6 84.8	83.9 " "	— — —	— — —
Cd(PhOx) ₂ 1H ₂ O	Jaune foncé	45	335	78.0	77.5	3.3	3.15
Ni(PhOx) ₂ 1H ₂ O	Jaune foncé	95	310	85.7 84.8 85.3	85.6 " "	3.9 3.35 —	3.48 " "
Co(PhOx) ₂ 1H ₂ O	Brun jaune**	95	295	84.4 84.4	84.5 "	3.75 4.1	3.48 "
Pb(PhOx) ₂ 2H ₂ O	Jaune	50	295	67.5	67.35	5.25	5.27
Hg(PhOx) ₂ anh.	Jaune orange	—	175	100	66.2	—	—
Mn(PhOx) ₂ 1H ₂ O	Brun clair	60	315	—	—	3.7	3.51
MoO ₂ (PhOx) ₂ anhydre	Jaune	—	300	75.6	74.7	—	—
Tl(PhOx) ₃ 1H ₂ O	Orange	50	190	75.7	76.8	2.0	2.04

* Par pesée. Toutes les autres valeurs ont été mesurées sur le papier photographique.

** Nuance très variable.

TABLEAU III

Chélate	Perte (%) par déshydratation		Nombre de moles H ₂ O	Θ_1 °C	Perte (%) par décomposition du chélate anhydre		Θ_2 °C	Mode de préparation
	Observée	Calculée			Observée	Calculée		
Cd(MeOx) ₂	0	—	0	—	70.15	70.05	310	a, b
Mn(MeOx) ₂	4.55	4.62	1	125	78.4	78.7	295	c
HgOx ₂ (?)	0	—	0	—	100	—	130	a, b
Hg(MeOx) ₂ (?)	3.5	3.4	1	45	100	—	~120	c
PbOx ₂	6.9	6.8	2	45	55.6	55.0*	280	b
"	3.9	3.5	1	130	57.9	58.2**	285	c
"	0	—	0	—	59.2	"	285	a
Pb(MeOx) ₂	4.3	3.33	1.3	45	58.4	57.4*	275	b
"	4.3	pour 1H ₂ O	1.3	45	58.3	—	275	c
"	4.2	—	1.3	55	57.5	60.2**	280	a

* Calculé pour PbO.

** Calculé pour Pb.

Le produit résiduel était tantôt PbO, tantôt Pb métal qui se réoxyde lentement.

a. Produit préparé à chaud selon le mode opératoire utilisé par BORREL ET PÂRIS⁴.

b. Produit préparé et filtré à froid, et séché par aspiration d'un courant d'air.

c. Mode de préparation intermédiaire: précipitation à 60-70°. Dans tous les cas, le milieu était tamponné à l'acétate d'ammonium.

III. CONCLUSIONS

Nos conclusions se présentent sous forme de tableaux ou de graphiques, où seront rassemblés les résultats de cette étude sur les phényl-2 oxinates et de celles déjà citées sur les oxinates et méthyl-2 oxinates, ces dernières étant d'ailleurs complétées par les résultats que nous présentons dans le Tableau III.

Le Tableau IV indique le nombre de molécules d'eau fixées sur chacun des chélates étudiés.

TABLEAU IV

Nombre de molécules H ₂ O	Al ³⁺	Mg ²⁺	Ni ²⁺	Co ²⁺	Zn ²⁺	Cd ²⁺	Cu ²⁺	Mn ²⁺	Hg ²⁺	Pb ²⁺	Tl ³⁺	Mo
Oxinates	0	2	2	2	2	2	2	2	0	0 à 2	1	$\frac{1}{2}$
Méthyl-oxi- nates	NC*	1	1	1	1	0	1	1	1	1,3	0	1/8
Phényl-oxi- nates	NC	NC	1	1	0	1	2	1	0	2	1	0

* NC: Ne donne pas de chélate.

Les températures θ_1 de début de déshydratation et θ_2 de début de décomposition des chélates des 3 réactifs sont portées sur les graphiques des Figs. 5 et 6. Les conclusions sont évidentes. Ainsi on notera que, sauf pour Hg, Pb et Tl, les chélates des deux dérivés substitués sont moins stables que les oxinates correspondants. Doit-on en conclure que l'accroissement de sélectivité obtenu en introduisant des substituants sur la molécule du réactif se paye par une perte de stabilité des chélates? Peut-être si l'on considère la stabilité thermique (résistance à la pyrolyse); mais cette stabilité thermique ne présente pas avec la stabilité ionique (dissociation en ions) une relation

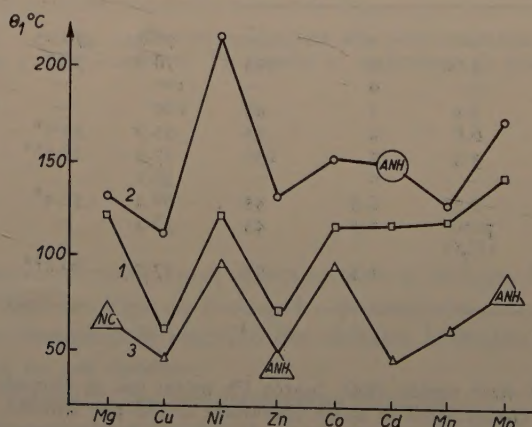


Fig. 5. Températures θ_1 de déshydratation des chélates.

Courbe 1: oxinates; courbe 2: méthyl-oxinates; courbe 3: phényl-2-oxinates.

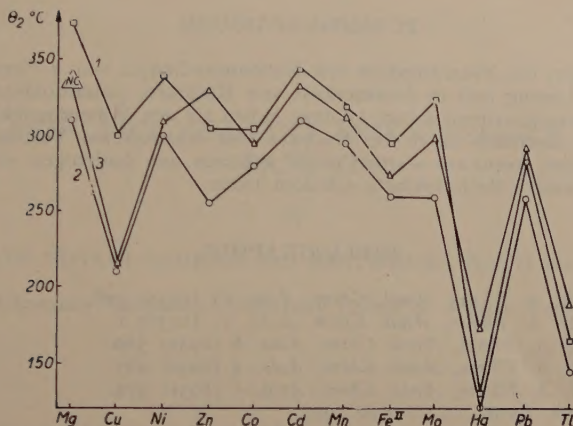


Fig. 6. Températures Θ_2 de début de décomposition des chélates.
 Courbe 1: oxinates; courbe 2: méthyl-2-oxinates; courbe 3: phényl-2-oxinates.

évidente. A ce sujet, la confrontation des divers résultats reproduits ci-dessus nous donnera l'occasion d'une remarque intéressante.

On sait qu'il existe une série des stabilités ioniques, valable pour les chélates de nombreux réactifs. Cette série, qui a été établie également dans le cas des oxinates^{7,8} et des méthyl-2 oxinates par JOHNSTON ET FREISER⁸, est la suivante (stabilités décroissantes): $\text{Hg} > \text{Cu} > \text{Ni} > \text{Pb} > \text{Zn}$ et $\text{Co} > \text{Cd} > \text{Fe}^{\text{II}} > \text{Mn} > \text{Mg} > \text{Ca}$ (a).

Or, si l'on effectue un classement analogue avec les stabilités thermiques des oxinates, méthyl-2 et phényl-2 oxinates, on obtient 3 séries dont la moyenne est (stabilités croissantes):

$\text{Hg} < \text{Cu} < \text{Fe}^{\text{II}} < \text{Pb} < \text{Zn} < \text{Co} < \text{Mn} < \text{Ni} < \text{Cd} < \text{Mg}$ (b).

Les séries (a) et (b) sont inverses: la stabilité thermique croît cependant que la stabilité ionique décroît.

Quel que soit le nombre d'exceptions que comporte chaque série particulière par rapport aux séries générales (a) et (b) — ces exceptions pouvant d'ailleurs être intéressantes à examiner de près — et en nous limitant à l'allure générale des phénomènes, nous pensons pouvoir affirmer que les chélates de l'oxine et de ses dérivés dont la stabilité ionique est la plus grande sont en général ceux qui résistent le moins bien à la pyrolyse.

RÉSUMÉ

Les auteurs ont étudié par potentiométrie les conditions de précipitation des phényl-2 oxinates, en milieu hydroalcoolique. Par analyse thermogravimétrique, ils ont ensuite déterminé le taux d'hydratation et les domaines de stabilité thermique de ces chélates. Ces résultats ont été comparés en outre avec ceux obtenus antérieurement pour les oxinates et les méthyl-2 oxinates.

SUMMARY

The authors have studied the potentiometric curves obtained during the neutralization, in dilute alcoholic media, of acid solutions containing 2-phenyl-8-quinolinol and metallic cations, with sodium hydroxide. By thermogravimetric analysis the number of water molecules and regions of stability for hydrates and anhydrous compounds were also established.

Moreover these results were compared with those previously obtained for oxinates and methyl-2 oxinates.

ZUSAMMENFASSUNG

Die Verfasser haben die Neutralisation mit Natriumhydroxyd von 2-Phenyloxin, in saurer hydroalkoholischer Lösung und in Anwesenheit von Kationen, potentiometrisch verfolgt.

Mit Hilfe der thermogravimetrischen Analyse haben sie den Wassermolekülgehalt sowie die Temperaturgrenzen innerhalb derer die Hydrate und wasserfreien Verbindungen beständig sind, festgestellt. Diese Resultate wurden unter anderem mit denjenigen verglichen, die man früher für Oxinate und 2-Methyloxinate erhalten hatte.

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STUDIES ON NESSLER'S REAGENT AND NESSLER'S PRECIPITATE
PART II

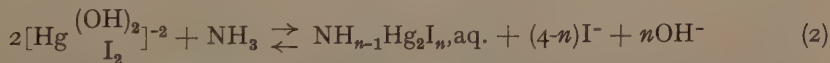
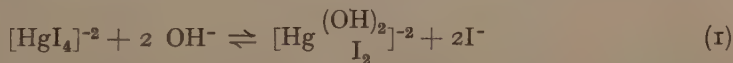
by

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For the detection of ammonia, NESSLER¹ first introduced a reagent, the preparation of which has subsequently been modified by different workers² — the presence of $[\text{HgI}_4]^{-2}$ ions being varied from 0.08M to 0.1M and the concentration of caustic alkalies from 0.5M to 3M. The existence of an intermediate compound has been shown in our previous communication³.

The composition of the characteristic brown precipitate, formed when the Nessler's reagent is treated with ammonia, has been described in the literature as $\text{NHg}_2\text{I}\cdot\text{H}_2\text{O}$ by some workers⁴ and as $\text{NH}_2\text{Hg}_2\text{I}_3$ by others⁵. In our present communication attempts have been made to arrive at a definite conclusion regarding its composition from potentiometric study, assuming that the formation of the precipitate takes place in the following manner:



Now if the initial molar concentration of $[\text{HgI}_4]^{-2}$ ions used be A , then,

$$A = A_1 + A_2 + 2A_3 \quad (3)$$

where A_1 and A_2 are the ultimate concentrations of $[\text{HgI}_4]^{-2}$ and $[\text{Hg} \begin{smallmatrix} (\text{OH})_2 \\ \text{I}_2 \end{smallmatrix}]^{-2}$ ions respectively and A_3 the number of moles of $\text{NH}_{n-1}\text{Hg}_2\text{I}_n, \text{aq.}$ precipitated from a litre of the Nessler's solution, due to addition of a known amount of ammonia, the concentration of which is denoted by a . Throughout the series of an experiment, the concentration (B) of potassium hydroxide has been assumed to remain constant as it was present in large excess. So the apparent equilibrium constant K' from (1) is given by,

$$K' = \frac{A_2 I^2}{A_1} \quad (4)$$

where I is the concentration of total iodide ion liberated.

And from (1) and (2), we have,

$$I = 2A_2 + (8-n)A_3 \quad (5)$$

As $\text{NH}_{n-1}\text{Hg}_2\text{I}_n\cdot\text{aq.}$ is practically insoluble and ammonia remaining unreacted is infinitely small, it can be deduced from (2),

$$A_3 = a. \quad (6)$$

From (3), (4), (5) and (6) by solving, the expression for n is given by,

$$n = 8 - \frac{1}{a} \left\{ I - \frac{2(A - 2a)}{1 + \frac{I^2}{K'}} \right\} \quad (7)$$

EXPERIMENTAL

The values of I , with or without addition of ammonia to the Nessler's reagent, were calculated from the observed e.m.f. of the concentration cells containing iodide-hypoiodite system, following similar procedure and using the reagents of the same grade as described in detail in our previous communication. The concentration of iodide ion in the reference cell was 0.02M. It was observed that when caustic alkalies of high concentration were present in the Nessler's reagent, there was a deposition of yellow HgO at the liquid junction of the KCl bridge during e.m.f. measurements. This difficulty had been avoided by replacing KCl in the bridge with KOH , the concentration of which was the same as that of the alkali present in the concentration cells, and the observed e.m.f. values were corrected as usual. In each case, knowing the value of I before adding ammonia, K' was calculated from the relation (4) and from the corresponding value of I , after adding a known amount of ammonia, n in (7) was evaluated. The results are stated in Table I. The amount of ammonia was added in such a proportion as to precipitate 16% of mercury initially present in the solution.

TABLE I
CONCENTRATION OF IODIDE ION IN THE REFERENCE CELL = 0.02M

Concn. of $[\text{HgI}_4]^{-2}$ A	Concn. of alkali B	E (corrected) in Volts Without ammonia	E (corrected) in Volts With ammonia	Concn. of ammonia a	$pA - 2pB$	n
0.05	3.03	0.0140	0.0165	0.004	2.26	0.8
0.10	3.03	0.0195	0.0225	0.008	1.96	1.0
0.20	3.03	0.0245	0.0285	0.016	1.66	1.2
0.05	2.02	0.0130	0.0155	0.004	1.91	1.0
0.10	2.02	0.0175	0.0210	0.008	1.61	1.1
0.20	2.02	0.0230	0.0275	0.016	1.31	1.3
0.05	1.00	0.0100	0.0130	0.004	1.30	1.3
0.10	1.00	0.0150	0.0190	0.008	1.00	1.5
0.20	1.00	0.0220	0.0265	0.016	0.70	1.8
0.05	0.49	0.0070	0.0105	0.004	0.68	1.8
0.10	0.49	0.0120	0.0165	0.008	0.38	2.3
0.20	0.49	0.0205	0.0245	0.016	0.08	2.9

From the experimental data, it has been observed that n is a function of both A and B . In order to find out any empirical relation between n , A and B , a curve (Fig. 1) has been obtained by plotting n against the corresponding values of $(pA - 2pB)$ and the following empirical relation has been derived,

$$n \left(\log_{10} \frac{B^2}{A} + 1 \right) = 3.$$

Another set of experiments was carried out by adding the different amounts of ammonia to the same solution of Nessler's reagent and the results are stated graphically in Fig. 2, by plotting n against logarithm of the percentage of mercury precipitated as ammoniated product. It has been found that the value of n increases with the increase in concentration of ammonia. The colour of the precipitate also deepens

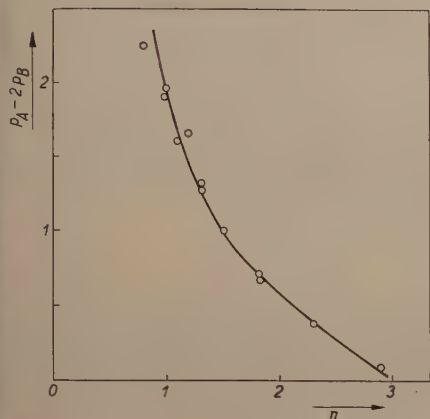


Fig. 1.

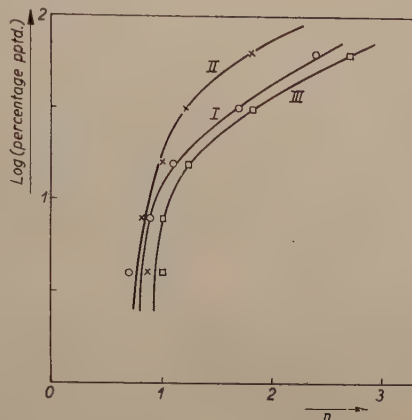
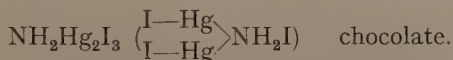
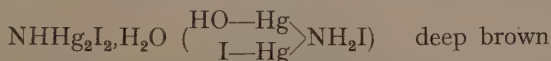
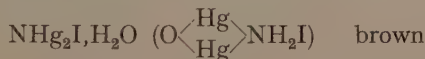


Fig. 2.

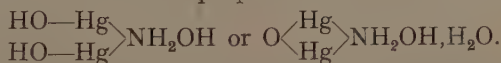
I — A = 0.1M; B = 2.01M
 II — A = 0.1M; B = 3.0M
 III — A = 0.2M; B = 3.01M

from brown to chocolate with the increase in iodine content and the chance of the formation of a precipitate containing no iodine is very remote.

Hence it may be concluded that the composition of the precipitate depends on the concentrations of $[\text{HgI}_4]^{-2}$ and OH^- ions as well as on the amount of ammonia added. The possible compositions are as stated below:



It may be of interest to recall the properties of Millon's Base⁶:

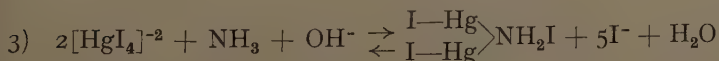
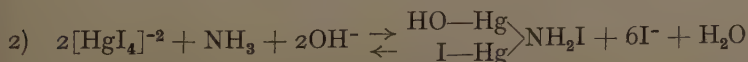
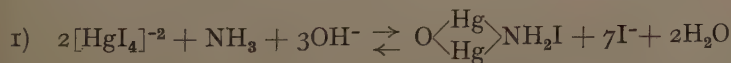


Ordinary salt solutions + Millon's Base \rightarrow Salts of Millon's Base (very difficultly soluble) + hydroxide of metal, *e.g.*

(i) Dilute KI solution + Millon's Base \rightarrow Iodide of Millon's base + KOH, the filtrate being free from iodide ion.

(ii) CuSO_4 or FeCl_3 solution shaken with Millon's Base gives rise to a filtrate free from all salts.

Therefore the suggested overall reactions are:



From the experimental data it may be observed that as the concentration of ammonia or iodomercurate ion increases, alkali remaining constant, the precipitate tends towards the formula $\text{NH}_2\text{Hg}_2\text{I}_3$; while when alkali concentration increases and the other reactants are constant, the formula of the precipitate approaches to $\text{NHg}_2\text{I}, \text{H}_2\text{O}$.

As the Nessler's reagent is mainly used for the detection or estimation of traces of ammonia, so it may be stated that the characteristic brown coloration or precipitation is due to the formation of $\text{NHg}_2\text{I}, \text{H}_2\text{O}$.

SUMMARY

The composition of the precipitate formed when the Nessler's reagent is treated with ammonia, is assumed as $\text{NH}_{n-1}\text{Hg}_2\text{I}_n$, aq. and has been studied potentiometrically from iodide-hypoiodite-system. It has been observed that the value of n depends on the concentrations of $[\text{HgI}_4]^{-2}$ and OH^- ions as well as on the amount of ammonia added and it may vary from 1 to 3. The colour of the precipitate deepens from brown to chocolate as the value of n increases.

RÉSUMÉ

Les auteurs attribuent au précipité, formé lorsque le réactif de Nessler est traité par l'ammoniaque, la formule suivante $\text{NH}_{n-1}\text{Hg}_2\text{I}_n$, aq. La formation de ce composé a été étudiée potentiométriquement à partir du système iodure-hypoiodite. On a constaté que la valeur de n dépend des concentrations des ions $[\text{HgI}_4]^{-2}$ et OH^- , ainsi que de la quantité d'ammoniaque ajoutée; elle peut varier de 1 à 3. La coloration du précipité fonce du brun au chocolat lorsque la valeur de n croît.

ZUSAMMENFASSUNG

Die Autoren geben dem Niederschlag, welcher sich bildet wenn man das Nessler'sche Reagenz mit Ammoniak behandelt, folgende Formel: $\text{NH}_{n-1}\text{Hg}_2\text{I}_n$, aq. Die Bildung dieser Verbindung wurde potentiometrisch vom System Jodid-Hypoiodit ausgehend untersucht. Man stellte fest, dass der Wert n von den Konzentrationen der Ionen $[\text{HgI}_4]^{-2}$ und OH^- , sowie auch von der Quantität des hinzugefügten Ammoniaks abhängt; er kann zwischen 1 und 3 variieren. Die Farbe des Niederschlages vertieft sich mit wachsendem Wert von n von braun zu schokoladebraun.

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VOLUMETRIC STUDIES IN OXIDATION-REDUCTION REACTIONS

VII. REDUCTION WITH FERROUS ETHYLENEDIAMINE SULPHATE

CERIC SULPHATE METHOD*

by

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CARAWAY AND OESPER¹ showed that ferrous ethylenediamine sulphate $\text{FeSO}_4 \cdot (\text{CH}_2\text{NH}_3)_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ reacted stoichiometrically with standard solutions of three powerful oxidizing agents, namely, potassium permanganate, potassium dichromate and ceric sulphate which are commonly employed in oxidimetric titrations.

SINGH² *et al.* have used ferrous ethylenediamine sulphate for the indirect volumetric estimations of potassium chlorate, potassium bromate, potassium metaperiodate, potassium dichromate, potassium ferricyanide, potassium permanganate, potassium persulphate, hydrogen peroxide and ceric sulphate. The excess of ferrous ethylenediamine sulphate added to each of the substances was titrated with standard potassium permanganate and also with standard potassium dichromate solution. In the present investigation the substances have been determined indirectly by a volumetric method using ferrous ethylenediamine sulphate as reducing agent. The excess of standard ferrous ethylenediamine sulphate solution added to each of the substances was titrated with standard ceric sulphate solution using ferroin as an indicator.

EXPERIMENTAL

A known weight of each substance was mixed with an excess of standard ferrous ethylenediamine sulphate solution and the mixture acidified with sulphuric acid to keep its normality between 1 and 2N. In the case of potassium chlorate and potassium bromate the normality of the mixture with respect to sulphuric acid was kept between 4 and 6N. The mixture containing potassium chlorate was heated to 80° C for about ten minutes in an atmosphere of carbon dioxide and then allowed to cool. In the case of potassium ferricyanide, 5 ml of freshly prepared solution of ferric chloride (containing 1.0 g per 100 ml), 20 ml of 1N HCl, 30 ml of water and excess of ferrous ethylenediamine sulphate solution were added. The precipitate of $\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$ formed, was filtered and thoroughly washed with water. The filtrate, containing the excess of ferrous ethylenediamine sulphate, was acidified with sulphuric acid. In each case the excess of ferrous ethylenediamine sulphate was titrated against standard ceric sulphate solution using ferroin as an indicator.

All chemicals, except ceric sulphate, used in this investigation were of guaranteed purity. Ceric sulphate was standardized with A.R. arsenious oxide³. Ferrous ethylenediamine sulphate was prepared by the method of CARAWAY AND OESPER¹.

* For Part VI of this series, see *Research Bull. Panjab Univ.*, (1955) 141.

The results given in Tables I to IX show that the substances can be determined indirectly by the volumetric method, using ferrous ethylenediamine sulphate (FES) as reducing agent in acid medium.

TABLE I

POTASSIUM CHLORATE

$KClO_3$ taken g	$N/20$ FES added ml	$N/20$ $Ce(SO_4)_2$ used for excess FES ml	$N/20$ FES used by $KClO_3$ ml	$KClO_3$ found g
0.0052	20.00	15.00	5.00	0.0051
0.0099	20.00	10.40	9.60	0.0098
0.0134	30.00	16.90	13.10	0.0133
0.0178	30.00	12.80	17.20	0.0176
0.0220	30.00	8.60	21.40	0.0219

TABLE II

POTASSIUM BROMATE

$KBrO_3$ taken g	$N/20$ FES added ml	$N/20$ $Ce(SO_4)_2$ used for excess FES ml	$N/20$ FES used by $KBrO_3$ ml	$KBrO_3$ found g
0.0068	20.00	15.00	5.00	0.0069
0.0138	20.00	10.00	10.00	0.0139
0.0207	30.00	15.00	15.00	0.0208
0.0276	30.00	10.00	20.00	0.0278
0.0346	45.00	20.00	25.00	0.0347

TABLE III

POTASSIUM METAPERIODATE

KIO_4 taken g	$N/20$ FES added ml	$N/20$ $Ce(SO_4)_2$ used for excess FES ml	$N/20$ FES used by KIO_4 ml	KIO_4 found g
0.0286	20.00	15.00	5.00	0.0287
0.0574	20.00	10.00	10.00	0.0575
0.0746	20.00	7.00	13.00	0.0747
0.0920	30.00	14.00	16.00	0.0920
0.1092	30.00	11.00	19.00	0.1092

TABLE IV

POTASSIUM DICHROMATE

$K_2Cr_2O_7$ taken g	$N/20$ FES added ml	$N/20$ $Ce(SO_4)_2$ used for excess FES ml	$N/20$ FES used by $K_2Cr_2O_7$ ml	$K_2Cr_2O_7$ found g
0.0123	30.00	25.05	4.95	0.0121
0.0240	30.00	20.10	9.90	0.0243
0.0339	30.00	16.10	13.90	0.0341
0.0416	30.00	13.00	17.00	0.0417
0.0487	30.00	10.05	19.95	0.0489

TABLE V

POTASSIUM FERRICYANIDE

$K_3[Fe(CN)_6]$ taken g	N/20 FES added ml	N/20 $Ce(SO_4)_2$ used for excess FES ml	N/20 FES used by $K_3[Fe(CN)_6]$ ml	$K_3[Fe(CN)_6]$ found g
0.0548	10.00	5.00	5.00	0.0549
0.1096	20.00	10.00	10.00	0.1097
0.1425	30.00	17.00	13.00	0.1426
0.1754	30.00	14.00	16.00	0.1756
0.2083	40.00	21.00	19.00	0.2085

TABLE VI

POTASSIUM PERMANGANATE

$KMnO_4$ taken g	N/20 FES added ml	N/20 $Ce(SO_4)_2$ used for excess FES ml	N/20 FES used by $KMnO_4$ ml	$KMnO_4$ found g
0.0078	20.00	15.00	5.00	0.0079
0.0156	20.00	10.00	10.00	0.0158
0.0204	20.00	7.00	13.00	0.0205
0.0252	25.00	9.00	16.00	0.0253
0.0300	35.00	16.00	19.00	0.0300

TABLE VII

POTASSIUM PERSULPHATE

$K_2S_2O_8$ taken g	N/20 FES added ml	N/20 $Ce(SO_4)_2$ used for excess FES ml	N/20 FES used by $K_2S_2O_8$ ml	$K_2S_2O_8$ found g
0.0337	20.00	15.00	5.00	0.0338
0.0674	20.00	10.00	10.00	0.0676
0.0877	20.00	7.00	13.00	0.0878
0.1080	20.00	4.00	16.00	0.1081
0.1281	25.00	6.00	19.00	0.1283

TABLE VIII

HYDROGEN PEROXIDE

H_2O_2 taken g	N/20 FES added ml	N/20 $Ce(SO_4)_2$ used for excess FES ml	N/20 FES used by H_2O_2 ml	H_2O_2 found g
0.0042	20.00	15.00	5.00	0.0043
0.0084	20.00	10.00	10.00	0.0085
0.0126	20.00	5.00	15.00	0.0128
0.0170	30.00	10.00	20.00	0.0170
0.0213	45.00	20.00	25.00	0.0213

TABLE IX

CERIC SULPHATE

$Ce(SO_4)_2$ taken g	N/20 FES added ml	N/20 $Ce(SO_4)_2$ used for excess FES ml	N/20 FES used by $Ce(SO_4)_2$ ml	$Ce(SO_4)_2$ found g
0.0830	20.00	15.00	5.00	0.0831
0.1660	20.00	10.00	10.00	0.1661
0.2325	20.00	6.00	14.00	0.2326
0.2990	30.00	12.00	18.00	0.2990
0.3654	30.00	8.00	22.00	0.3654

SUMMARY

Ferrous ethylenediamine sulphate has been used as a reducing agent in acid medium for the indirect volumetric estimations of potassium chlorate, potassium bromate, potassium metaperiodate, potassium dichromate, potassium ferricyanide, potassium permanganate, potassium persulphate, hydrogen peroxide and ceric sulphate. The excess of ferrous ethylenediamine sulphate added to each of the substances in acid medium was titrated with standard ceric sulphate solution using ferroin as an indicator.

RÉSUMÉ

Le sulfate double de fer(II) et d'éthylènediamine a été utilisé comme réducteur en milieu acide, pour les dosages volumétriques indirects du chlorate, du bromate, du métaperiodate, du dichromate, du ferricyanure, du permanganate et du persulfate de potassium, du peroxyde d'hydrogène et du sulfate cérique. L'excès de réactif ajouté à chacune de ces substances est titré par une solution étalon de sulfate de cérium(IV) en milieu acide, en présence de ferroïne comme indicateur.

ZUSAMMENFASSUNG

Das Doppelsalz aus Eisen(II) und Äthylendiaminsulfat wurde in saurem Milieu als Reduktionsmittel verwendet für indirekte volumetrische Bestimmungen von Kaliumchlorat, -bromat, -metaperiodat, -bichromat, -ferricyanid, -permanganat und -persulfat, Wasserstoffperoxyd und Cersulfat. Der Überschuss des zu jeder dieser Substanzen zugegebenen Reagenzes wird mit einer Titerlösung von Cer(IV)sulfat in saurer Lösung in Gegenwart von Ferroin als Indikator titriert.

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OXIDATIONS WITH ALKALINE PERMANGANATE USING MONOVALENT THALLIUM FOR THE BACK-TITRATION

II. DETERMINATION OF IODATE, IODIDE AND FERROCYANIDE

by

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In estimating iodate and iodide STAMM¹, HEREDIA² and SINGH³ oxidized them with potassium permanganate in alkaline medium, and back-titrated the excess oxidant with formate. In this investigation, monovalent thallium was used as a substitute for sodium formate⁴ and a study was made of the oxidation of the above materials and of ferrocyanide with alkaline permanganate.

EXPERIMENTAL

Solutions of the substances to be oxidized, (*viz.* iodide, iodate⁵ and ferrocyanide⁶) were prepared from the AnalaR or recrystallized products. Their solutions were standardized according to recommended procedures^{5,6}.

The experimental technique is the same as previously described⁷. The reactions to be described below consist of:

- the direct oxidation of the reducing substance in alkaline solutions with KMnO_4 ,
- titration of KMnO_4 with the reducing material in presence or absence of Ba^{+2} ions,
- oxidation of the reductant with KMnO_4 and back-titration of excess oxidant with monovalent thallium.

RESULTS

I. Oxidation of iodate with alkaline permanganate

On titrating KMnO_4 with iodate in absence of Ba^{+2} ions, the reaction products are periodate and manganate. The inflection at the end-point is very poor, amounting

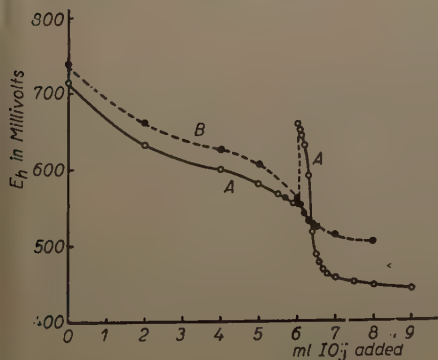


Fig. 1.

(A) 25 ml 0.1261N KMnO_4 , 2N NaOH titrated with 0.0992N IO_3^- , Ba^{+2} added just before end-point.

(B) Same as (A) with no Ba^{+2} .

to ~ 12 mV in the presence of $3N$ NaOH (*cf.* Fig. 1 B). At lower alkalinity no apparent inflection was observed characterizing the end-point.

In the presence of Ba^{+2} ions on the other hand, the inflections are sharper amounting to ~ 70 – 80 mV but the end-points are always attained late. This is possibly due to the precipitation of $Ba(IO_3)_2$ which escapes oxidation. The amount of the precipitated iodate apparently increases by increasing the concentration of Ba^{+2} present, leading to still later end-points. On slowly stirring the solution, the precipitated iodate settles down and the equilibria are rapidly attained. If on the other hand the stirring is vigorous, the time for equilibrium increases on account of the oxidation of the precipitated salt. Better results could be obtained by performing the titrations in $2N$ NaOH in the absence of Ba^{+2} ions, the latter being added only just before the end-point, when a sudden rise in potential occurs (*cf.* Fig. 1 A). On continuing the titration a sharp inflection is observed at the end-point. The latter deviates only slightly from the theoretical values when $0.1N$ solutions are used, but the deviation increases with dilution of the iodate solution.

TABLE I
TITRATION OF 25 ml $0.1261N$ $KMnO_4$ WITH IO_3^-

Alkalinity	Vol. of 5% Ba^{+2}	Max. inflec. per 0.1 ml IO_3^-	Theor. end-point	Exptl. end-point	Error
$IO_3^- = 0.0992N$					
3N NaOH	—	12 mV	6.36 ml	6.15 ml	3.3 %
1.5N	6 ml	19	6.36	6.57	—3.3
1.5N	10	80	6.36	6.82	—7.27
2N	10 *	103	6.36	6.385	—0.39
2N	8 **	74	6.36	6.325	0.55
$IO_3^- = 0.0496N$					
2N	10 ml ***	66 mV	12.72 ml	12.58 ml	1.1 %

* Ba^{+2} added 0.4 ml before end-point.

** Ba^{+2} added 0.1 ml before end-point.

*** Ba^{+2} added 0.6 ml before end-point.

II. Oxidation of iodide

On titrating $KMnO_4$ with iodide, the latter is oxidized either to iodate or periodate, depending on whether Ba^{+2} ions are absent or present. In presence of Ba^{+2} ions the end-points are attained with considerable jumps (*cf.* curve A, Fig. 2) which can be decreased by decreasing the concentrations of solutions and the quantity of Ba^{+2} present. As is apparent from the data shown in Table II, the results vary according to the concentration of the reactants, the errors amounting to 0.5–0.63% in case of the $0.1N$ solutions, and increase when the concentrations are lowered. In absence of Ba^{+2} ions a smaller jump is observed which corresponds to the oxidation of I^- to IO_3^- (curve B, Fig. 2), the periodate formed being possibly reduced by the titrant⁶.

In both cases the reaction is slow, needing ~ 5 – 10 min at the beginning and 30 min at the end-point. Attempts to accelerate the reaction by using HgO , ZnO , Ni^{+2} , and Au^{+3} ions were futile.

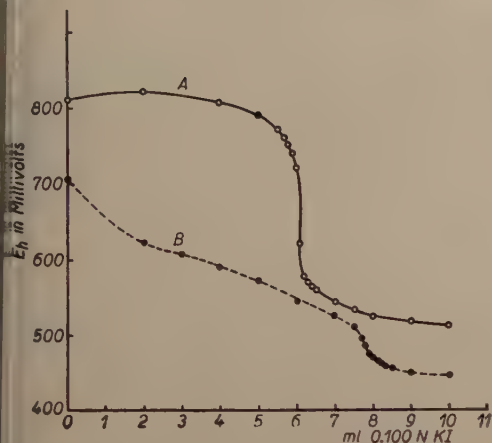


Fig. 2. Titration of 25 ml 0.1203N KMnO_4 with 0.1000N KI.

(A) 0.5N NaOH + Ba^{+2} ions
(B) 2N NaOH

In the direct titration of I^- with KMnO_4 in presence of Ba^{+2} ions a jump amounting to ~ 70 mV is observed at the end-point, which corresponds to the oxidation of $\text{I}^- \rightarrow \text{IO}_3^-$. The errors in this case are considerable, ranging from 3-5% in 1-3N NaOH and the reaction is slower than the reverse titration of KMnO_4 with I^- .

TABLE II

TITRATION OF KMnO_4 WITH I^- IN PRESENCE OF Ba^{+2} IONS

Alkalinity	Max. inflec. per 0.1 ml I^-	Vol. of 5% Ba^{+2}	Theor. end-point	Exptl. end-point	Error
25 ml 0.1203N KMnO_4 titrated with 0.1N I^- :					
1N NaOH	108 mV	10 ml	6.02 ml	6.05 ml	-0.5 %
0.5N	96	10	6.02	6.04	-0.33
25 ml 0.1261N KMnO_4 titrated with 0.05N I^- :					
0.5N NaOH	62 mV	10 ml	12.62 ml	12.73 ml	-0.91
25 ml 0.02406N KMnO_4 titrated with 0.01N I^- :					
1N NaOH	24 mV	3 ml	12.04 ml	11.35 ml	5.73
0.5N	16	3	12.04	11.9	1.16

TABLE III

TITRATION OF KMnO_4 WITH I_2 - I^- MIXTURE

Alkalinity	Vol. of 5% Ba^{+2}	Max. inflec. per 0.1 ml titrant	Theor. end-point	Exptl. end-point	Error
25 ml of 0.1631N KMnO_4 titrated with 0.0822N I_2 + 0.05N I^- :					
1N NaOH	—	18 mV	9.43 ml	9.48 ml	-0.53 %
1N	10 ml	59	7.07	7.065	0.07
0.5N	10	47	7.07	7.015	0.78
0.5N	10	50	7.07	7.06	0.14
0.8N	10	64	7.07	7.00	0.99

III. Oxidation of iodine in potassium iodide

As may be seen from the data shown in Table IV and Fig. 3, results similar to those found with iodide are obtained when a solution of I_2 in KI is used as the titrant. In presence of Ba^{+2} ions the oxidation of both ingredients yields IO_4^- , whereas in absence of Ba^{+2} they yield iodate. These reactions are somewhat more rapid than with the iodide alone, needing 5-6 min and 20 min at the beginning of the titration and at the end-point respectively.

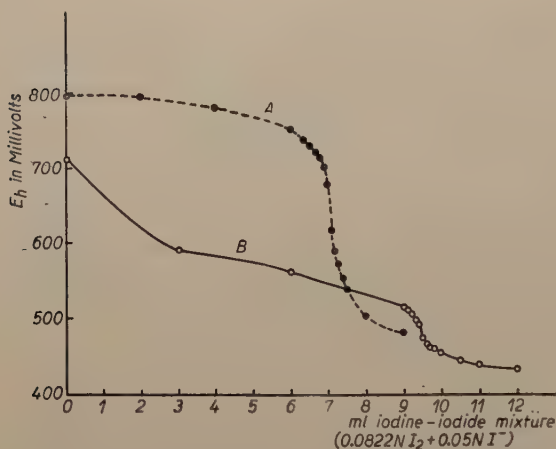


Fig. 3. Titration of 25 ml 0.1163N $KMnO_4$ in 1N NaOH with (0.0822N I_2 + 0.05N KI). (A) in presence of Ba^{+2} ions (B) in absence of Ba^{+2} ions

IV. Oxidation of ferrocyanide

In the oxidation of ferrocyanide with $KMnO_4$ in acid medium precipitation of manganous ferrocyanide occurs if the acid concentration is not sufficiently high, yielding inaccurate results⁶. It was thought that this difficulty could be overcome by performing the titrations in alkaline medium where reduction of $KMnO_4$ is checked at the MnO_2 stage. On titrating $K_4[Fe(CN)_6]$ solution free from acid or alkali the end-points are attained 1% earlier than the theoretical values. The errors increase on making the solution slightly acid but decrease on making it somewhat alkaline. Better results could be obtained in presence of telluric acid or sodium tellurate and 0.025-0.1N NaOH. At higher alkalinities than 0.1N, reduction of MnO_4^- yields MnO_4^{2-} without a characteristic inflection. The reaction is more or less rapid in absence of alkali but slows very much when alkali is added.

The titration curves (Fig. 4) are smooth but the inflections at the end-points are not very sharp, amounting to 20-30 mV per 0.1 ml $KMnO_4$.

Titration of $KMnO_4$ with ferrocyanide gives rise to manganate and contrary to the reverse process equilibria are rapidly attained. In absence of Ba^{+2} ions, the inflection at the end-point is not sharp but becomes distinct amounting to 50-80 mV in presence of Ba^{+2} ions (*cf.* Fig. 5).

The difficulty with this reaction is that the position of the end-point varies with the rate of adding the titrant (*cf.* Table IV A). However, satisfactory results could be obtained by slowly adding the titrant in presence of 0.5-1N NaOH and Ba^{+2} ions twice or $1\frac{1}{2}$ times equivalent to the manganate formed in the reaction. However, the

errors increase on decreasing the concentration of the reactants, owing perhaps to the partial dissociation of dilute ferrocyanide in the alkaline solution, whereby the free cyanide takes part in the reduction of KMnO_4 . Larger errors were also observed when the ferrocyanide solution was prepared from the non-crystallized AnalaR samples.

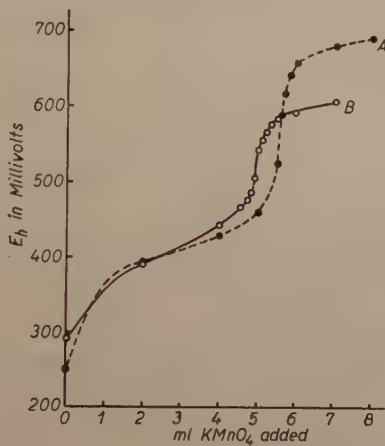


Fig. 4.

- (A) Titration of 5 ml 0.0814*N* ferrocyanide, 0.05*N* NaOH + telluric acid with 0.1192*N* KMnO_4 .
(B) Titration of 5 ml 0.0863*N* ferrocyanide, no alkali, with 0.1438*N* KMnO_4 .

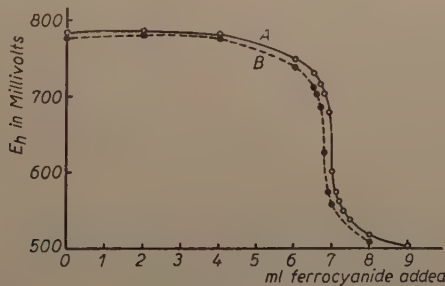


Fig. 5.

- (A) Titration of 25 ml 0.1204*N* KMnO_4 with 0.0863*N* ferrocyanide in 1*N* NaOH + Ba^{+2} ions.
(B) Titration of 10 ml 0.1204*N* KMnO_4 with 0.0353*N* ferrocyanide, 1*N* NaOH + Ba^{+2} ions.

TABLE IV A

TITRATION OF 25 ml 0.1204*N* KMnO_4 WITH 0.0925 FERROCYANIDE IN PRESENCE OF Ba^{+2} IONS

Alkalinity	Vol. of 5% Ba^{+2}	Rate of adding titrant	Max. inflec. at end-point	Theor. end-point	Exptl. end-point	Error
0.5 <i>N</i> NaOH	7 ml	slow	86 mV	6.5 ml	6.455 ml	0.69 %
0.5 <i>N</i>	7	rapid	62	6.5	6.67	—2.62
1.5 <i>N</i>	7	slow	64	6.5	6.36	2.15
1.5 <i>N</i>	7	rapid	60	6.5	6.75	—1.15
1 <i>N</i>	5	slow	50	6.5	6.44	0.92
1 <i>N</i>	10	slow	61	6.5	6.47	0.42

TABLE IV B
TITRATION OF KMnO_4 WITH FERROCYANIDE (ADDED SLOWLY) IN PRESENCE OF
 Ba^{+2} IONS AND 1N NaOH

Vol. and Normality of KMnO_4	Normality of ferrocyanide	Vol. of 5% Ba^{+2}	Max. inflec. per 0.1 ml titrant	Theor. end- point	Exptl. end- point	Error
25 ml 0.1204N	0.0863	7 ml	80 mV	6.98 ml	6.955 ml	0.36 %
25 ml 0.12 4N	0.0706	7	69	8.53	8.54	-0.12
10 ml 0.1204N	0.0353	7	58	6.82	6.79	0.44
25 ml 0.02408N	0.0212	2	60	5.68	5.58	1.76
25 ml 0.02408N	0.01412	2	21	8.53	8.23	3.52

TABLE V
TITRATION OF FERROCYANIDE WITH PERMANGANATE

Acidity or Alkalinity	Max. inflec. per 0.1 ml KMnO_4	Theor. end-point	Exptl. end-point	Error
5 ml 0.0746N $\text{K}_4[\text{Fe}(\text{CN})_6]$ diluted twice and titrated with 0.1192N KMnO_4 :				
1.5 · 10 ⁻¹ N H_2SO_4	27 mV	5.22 ml	5.04 ml	-3.45 %
1.5 · 10 ⁻⁴ N	31	5.22	5.06	-3.07
1.5 · 10 ⁻⁶ N	25	5.22	5.14	-1.35
1.5 · 10 ⁻⁷ N	27	5.2	5.15	-0.96
— (aqueous)	27	5.22	5.15	-0.96
5 ml 0.0814N $\text{K}_4[\text{Fe}(\text{CN})_6]$ diluted twice and titrated with 0.1192N KMnO_4 :				
0.05N NaOH	16 mV	5.69 ml	5.63 ml	-1.05 %
0.025N NaOH + telluric acid	29	5.69	5.65	-0.7
0.1N NaOH	27	5.69	5.734	0.77
0.025N NaOH + sodium tellurate ($\text{KMnO}_4 = 0.1246\text{N}$)	20	5.44	5.46	0.37

V. Oxidation with permanganate and back-titrating excess oxidant with monovalent thallium

The process consists in the oxidation of a given volume of the substance to be estimated by a known excess of KMnO_4 in presence of 1N NaOH and Ba^{+2} ions equivalent to the permanganate present.

The excess KMnO_4 is then titrated with monovalent thallium. This latter reagent was preferred to formate and formic acid on account of the rapidity of its reaction with KMnO_4 .

In the estimation of iodate by mixing with KMnO_4 in 1N NaOH and in presence of Ba^{+2} ions erroneous results were obtained, apparently due to partial precipitation of $\text{Ba}(\text{IO}_3)_2$ which escapes oxidation. Better results can be obtained when the oxidation of the iodate is performed in absence of Ba^{+2} ions, the latter being added just before titrating excess KMnO_4 with Tl^+ .

In trying to determine the excess of KMnO_4 after oxidizing ferrocyanide with formic acid, the reaction was very slow and the errors considerable. Tl^+ was therefore applied and the reaction then occurred rapidly. Good results can be obtained if the excess KMnO_4 is back-titrated immediately after mixing.

From the above study it becomes apparent that oxidation of iodate, iodide and iodine with permanganate is beset with many difficulties on account of the following facts:

- the smallness of the inflections in absence of Ba^{+2} ions,
- the precipitation of $\text{Ba}(\text{IO}_3)_2$ when Ba^{+2} ions are added,
- the tendency of I^- to give different oxidation products, *viz.* IO_3^- and IO_4^- .

Further studies will be made in an attempt to overcome these difficulties.

TABLE VI

<i>Vol. of reductant added</i>	<i>Theor. end-point</i>	<i>Exptl. end-point</i>	<i>Error</i>
25 ml 0.1291 <i>N</i> KMnO_4 mixed with 0.0992 <i>N</i> IO_3^- , and excess oxidant titrated with 0.0369 <i>N</i> Ti^{+} :			
3 ml IO_3^- *	9.46 ml	10.06 ml	-6.34 %
3 **	9.46	9.55	-0.95
3 **	9.46	9.54	-0.85
25 ml 0.1294 <i>N</i> KMnO_4 mixed with 0.1 <i>N</i> I^- , and excess oxidant titrated with 0.0369 <i>N</i> Ti^{+} :			
3 ml I^-	9.40 ml	9.34 ml	0.64 %
25 ml 0.1246 <i>N</i> KMnO_4 mixed with 0.0814 <i>N</i> $[\text{Fe}(\text{CN})_6]^{-4}$, and excess oxidant titrated with 0.0369 <i>N</i> Ti^{+} :			
5 ml $[\text{Fe}(\text{CN})_6]^{-4}$	5.83 ml	5.825 ml	0.09 %
5	5.83	5.872	-0.77
3	10.25	10.2	0.49
1	14.67	14.72	-0.34
5 ***	5.83	5.735	1.63

* Ba^{+2} added from beginning.

** Ba^{+2} added after mixed with iodate, oxidant titrated immediately after mixing.

*** Titration of oxidant half-an-hour after mixing.

SUMMARY

Iodate, iodide, iodine and ferrocyanide can be estimated by oxidation with KMnO_4 in alkaline media; the excess is back-titrated with Ti^{+} . I^- and I_2 are oxidized to IO_4^- in the presence of Ba^{+2} ions but only to IO_3^- in absence of such ions. The direct titration of IO_3^- , I^- with KMnO_4 proved valueless.

Ferrocyanide is oxidized by KMnO_4 in alkaline solutions and MnO_2 is formed. In the presence of telluric acid and 0.025-0.1*N* NaOH satisfactory results are obtained. Reduction of MnO_4^- with ferrocyanide gives MnO_4^{2-} and the results are variable, depending on the rate of adding the ferrocyanide.

RÉSUMÉ

Les iodates, iodures, ferrocyanures et l'iode peuvent être dosés par oxydation au moyen de KMnO_4 , en milieu alcalin; on titre l'excès de permanganate par le thallium(I). I^- et I_2 sont oxydés en iodate en l'absence de Ba^{+2} , et en periodate, en présence de Ba^{+2} . Dans le cas de l'oxydation des ferrocyanures, il y a formation de MnO_2 . En présence d'acide tellurique, dans NaOH 0.025 à 0.1*N*, les résultats sont satisfaisants. Cependant, dans le cas de la réduction du KMnO_4 par les ferrocyanures, il y a formation de MnO_4^{2-} , les résultats dépendant de la vitesse d'addition du ferrocyanure.

ZUSAMMENFASSUNG

Die Jodate, Jodide, Ferrocyanide und das Jod können mittels einer Oxydation mit Hilfe von KMnO_4 in alkalischer Lösung bestimmt werden. Man titriert den Überschuss des Permanganates mit Thallium(I). J^- und J_2 werden in Abwesenheit von Ba^{+2} zu Jodat oxydiert und in Gegenwart

von Ba^{+2} zu Perjodat. Im Falle der Oxydation der Ferrocyanide wird MnO_2 gebildet. Die Resultate sind in Gegenwart von Tellursäure in 0.025 bis 0.1N NaOH befriedigend. Im Falle der Reduktion des KMnO_4 durch Ferrocyanid dagegen, wird MnO_4^{-2} gebildet und die Ergebnisse hängen von der Zugabegeschwindigkeit des Ferrocyanides ab.

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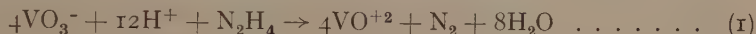
BROMOMETRIC DETERMINATION OF VANADIUM(V) BY HYDRAZINE

by

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Reduction of vanadium(V) to vanadium(IV) by hydrazine sulphate in sulphuric acid was studied by HOFMANN AND KÜSPERT¹ and the method was adopted for the gasometric and oxidometric determination of hydrazine. It was found that hydrazine is oxidized by vanadium(V) to nitrogen and water according to equation (1).



Later investigations of this reaction by BROWNE AND SHETTERLY² revealed the occurrence of a partial side reaction resulting in the formation of hydronitric acid and ammonia.



They observed that the extent of this side reaction depends on sulphuric acid concentration and temperature. The gasometric procedure gave an average negative error of about 4%, whereas the oxidometric procedure which consisted of the oxidation of vanadium(IV) formed by KMnO_4 , showed an error of less than 1%. The reduction of the error in the latter case was attributed to the oxidation of hydronitric acid by KMnO_4 . BRAY AND CUY³ confirmed the above findings and discarded the use of vanadium(V) for the estimation of hydrazine.

In a study of the oxidation of hydrazine by bromate and permanganate KOLTHOFF⁴ inferred that these reactions proceed smoothly according to equation (1) in sufficiently high concentration of hydrochloric acid, while the side reaction (2) occurs to some extent in dilute sulphuric acid. It seemed, therefore, that the occurrence of the side reaction in the reduction of vanadium(V) by hydrazine may be suppressed by maintaining high concentration of hydrochloric acid.

WILLARD AND YOUNG⁵ described a method for determining vanadium in chromium-vanadium steels by preferential oxidation of vanadium(IV) in presence of Cr(III) by potassium bromate. In the actual procedure the solution of the sample (in sulphuric acid), containing 10-20 mg vanadium, is heated for 15 minutes at 50-60° C with 2 to 3 g of potassium bromate in presence of hydrochloric acid and ammonium sulphate. The excess bromate is destroyed by boiling the solution and

vanadium(V), which is formed, is titrated against standard FeSO_4 . Preliminary tests in these laboratories showed that the oxidation of vanadium(IV) by bromate was very slow at room temperature and that in mixed solution containing vanadium(IV) and hydrazine the latter could be preferentially titrated against bromate in hydrochloric acid medium.

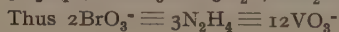
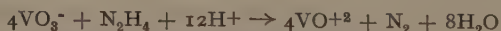
The bromometric determination of vanadium(V) by hydrazine consisted, therefore, of the reduction of vanadium(V) by a known excess of hydrazine in presence of sufficient hydrochloric acid to vanadium(IV) and the titration of excess hydrazine against standard potassium bromate.

The dead-stop end-point procedure of FOULK AND BAWDEN⁶, because of the speed, accuracy and easy detection of the end-point, was adopted for the titration of hydrazine against potassium bromate, in place of the classical dyestuff indicator method⁴.

EXPERIMENTAL

Stock solutions of vanadium(V) were prepared by accurately weighing out the requisite amount of vanadium pentoxide (E. Merck) and dissolving it in sodium carbonate (AnalaR). The vanadium content of an aliquot of the solution as determined by reduction of vanadium(V) by a known excess of FeSO_4 , and back titration of the excess FeSO_4 against standard $\text{Ce}(\text{SO}_4)_2$ or KMnO_4 in high concentration of sulphuric acid, using ferroin as indicator (*cf.* WILLARD AND YOUNG⁷) showed a close agreement with that calculated from the weight of vanadium pentoxide. Hydrazine sulphate solution was prepared by dissolving the necessary quantity of AnalaR sample in water. Its strength was determined by titration against standard KBrO_3 using the dead-stop end-point procedure.

Aliquot of vanadium(V) solution was taken in a 400 ml beaker, acidified with HCl and known excess of hydrazine sulphate solution was added to it. The overall acid normality was 4-5*N*. The solution was stirred and allowed to stand for 15 minutes. The dead-stop end-point titration unit was a simple manual type of apparatus with two identical platinum electrodes, a mechanical stirrer, and a sensitive galvanometer with adjustable shunt as employed by FOULK AND BAWDEN (*loc. cit.*). The potential applied across the electrodes was 10-20 millivolts. After adding about 2 g of potassium bromide to the mixed solution the stirrer was started and the excess hydrazine was titrated against standard KBrO_3 . Sufficient hydrochloric acid was added to maintain the acidity above 4-5*N* as recommended by KOLTHOFF (*loc. cit.*). The approach of the end-point was characterized by the temporary shift in the deflection of the galvanometer, with almost instantaneous return to the original position, after each addition of KBrO_3 . The end-point was indicated by a sharp and permanent kick in the galvanometer deflection. The bromate equivalent of hydrazine added, was similarly determined. The difference of the two bromate titer values gave directly the amount of vanadium(V) in terms of standard KBrO_3 . One ml of potassium bromate (0.1*N*) corresponds to 0.005095 g vanadium. The relation is based on the following considerations:



Since the equivalent weight of bromate is 1/6 its molecular weight,
1 g equivalent of bromate \equiv 1 g atom of vanadium.

Table I shows a typical set of results.

The close agreement between the observed and the calculated values for the vanadium content, substantiates the observation that under the given operative conditions vanadium(IV) is not oxidized by KBrO_3 and that the present method may therefore be adopted for the quantitative estimation of vanadium(V).

TABLE I

Expt. No.	Vol. of vanadium solution ml	Hydrazine added ml	KBrO ₃ for excess hydrazine ml	KBrO ₃ for hydrazine added ml	Normality of KBrO ₃	Amount of vanadium g		Difference g
						Found	Taken	
1	25	10	36.70	51.00	0.03863N	0.02814	0.02800	+0.00014
2	20	10	33.80	50.80	0.03863N	0.03345	0.03364	-0.00019
3	20	10	10.85	19.60	0.1000N	0.04457	0.04472	-0.00015
4	25	20	28.15	39.20	0.1000N	0.05628	0.05590	+0.00038
5	50	10	22.55	51.00	0.03863N	0.05600	0.05600	nil
6	40	10	16.50	50.80	0.03863N	0.06750	0.06726	+0.00024
7	75	10	8.65	51.00	0.03863N	0.08333	0.08400	-0.00067
8	50	20	14.45	36.50	0.1000N	0.1123	0.1118	+0.00050

Our sincere thanks are due to Professor S. S. JOSHI for facilities and kind interest in the work.

SUMMARY

A method for the quantitative determination of vanadium(V), based on the reduction of vanadium(V) by hydrazine, has been described. The reduction is carried out in high concentration of hydrochloric acid and the excess hydrazine back-titrated against standard potassium bromate, using the dead-stop end-point procedure. Hydrazine is preferentially oxidized by bromate in presence of vanadium(IV). Accurate results have been obtained over a wide range of vanadium(V) concentration.

RÉSUMÉ

Une méthode de dosage du vanadium basée sur la réduction du vanadium(V) par l'hydrazine est décrite. Cette réduction est effectuée dans l'acide chlorhydrique en forte concentration; l'excès d'hydrazine est titré en retour par une solution étalon de bromate de potassium, par la méthode du "dead-stop". L'hydrazine s'oxyde, par le bromate, plus facilement que le vanadium(IV). Des résultats précis ont été obtenus pour des concentrations très différentes de vanadium(V).

ZUSAMMENFASSUNG

Es wird eine Methode zur Bestimmung von Vanadium beschrieben, welche auf der Reduktion des Vanadium(V) mit Hydrazin beruht. Diese Reduktion wird in stark konzentrierter Salzsäure ausgeführt. Der Überschuss an Hydrazin wird mit einer Vergleichslösung von Kaliumbromat nach der „dead-stop“ Methode zurücktitriert. Das Hydrazin wird durch Bromat leichter oxydiert als Vanadium(IV). Es wurden genaue Resultate für sehr verschiedene Konzentrationen an Vanadium(V) erhalten.

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ANALYSIS OF STYRENATED METHYL ESTERS OF LINSEED OIL FATTY ACIDS BY MOLECULAR DISTILLATION

by

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INTRODUCTION

Though much attention has been paid in recent years to the reaction of styrene with drying oils, little is yet known about the nature of the reaction products. Most of the work done deals with the separation of high-molecular polystyrene from styrenated oils by precipitation methods. The lack of a method whereby a good separation of the reaction products can be effected without changing the nature of the products is one of the main difficulties.

PETIT AND FOURNIER¹ subjected the mixture of fatty acids which remained after the removal of polystyrene from styrenated linseed and tung oil to a distillation at pressures ranging from 2 to 5 mm Hg. They claimed the isolation of a fraction which contained one mole styrene per mole fatty acid which they supposed to be a Diels-Alder adduct (styrene reacting as a dienophile). As considerable cracking took place during the distillation, the determination of the styrene content based on determination of acid values is not reliable. Unstyrenated oils subjected to the same treatment gave fractions the acid values of which differed much from the original fatty acids.

A way to avoid the degradation of the products is the use of molecular distillation of the esters rather than normal vacuum distillation of the free acids.

EXPERIMENTAL PART

The molecular still used was of the cascade fractionating-type as described by ALDERSHOFF, BOOY, LANGEDIJK, PHILIPPI AND WATERMAN². The high separating power is due to nine stages of vaporization and condensation. The still proper and the vacuum system were constructed as separate units, each unit being transportable to permit easier handling of the apparatus. The molecular still and the vacuum system are shown diagrammatically in Fig. 1. A photograph of the assembly is shown in Fig. 2.

Determination of the separating power

An idea of the separating efficiency was obtained by determining the plate number of the still using the data of BOOY *et al.*² who distilled a mixture of di-*n*-butyl phthalate and di-*n*-butyl

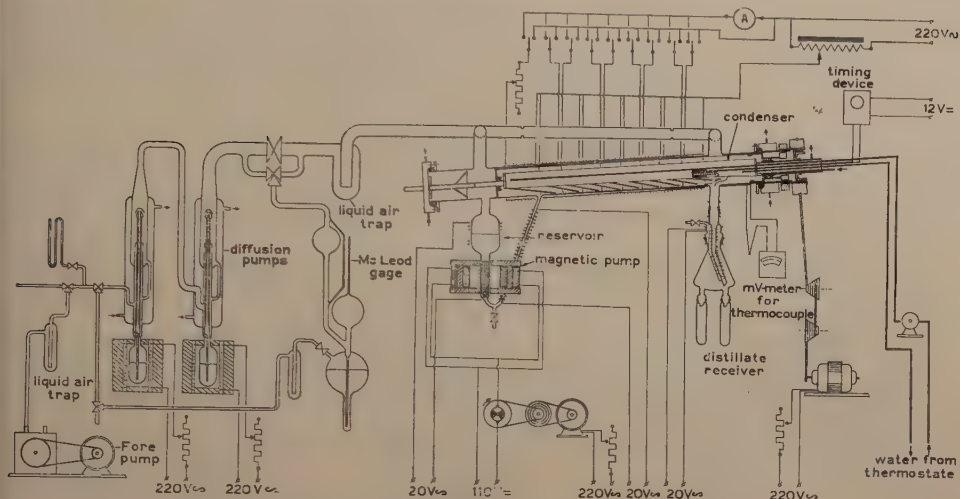


Fig. 1. Diagram of cascade fractionating molecular still.

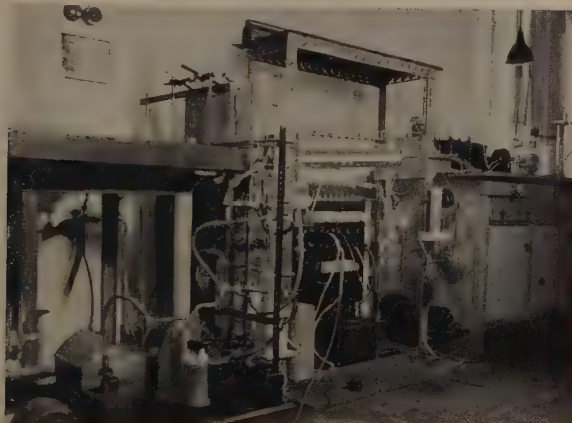


Fig. 2. Cascade fractionating molecular distillation equipment.

azelate in a similar apparatus. The plate number was determined by the McCabe-Thiele graphical procedure because the deviation from constant relative volatility was too great to permit the algebraic method of Fenske. The equilibrium curve was drawn according to data from WILLIAMS³ who determined the vapour-liquid equilibrium of this system at 1 mm Hg.

The results are summarized in Table I.

TABLE I

DISTILLATION OF MIXTURES OF DI-*n*-BUTYL PHTHALATE AND DI-*n*-BUTYL AZELATE
Temp.: 68° C; pressure: $<10^{-4}$ mm Hg; total reflux.

Still composition mole % phthalate	Distillate composition mole % phthalate	Plate number
19.5	80.0	12
32.2	78.1	9

The degree of separation attained in the molecular still is thus the same as can be achieved by distilling this particular mixture at 1 mm pressure using a column of 9 to 12 theoretical plates.

As we were mainly concerned with the problem of separating unreacted methyl esters of fatty acids from addition compounds with styrene, a trial distillation of a mixture of two model-compounds was performed. Methyl oleate and benzyl oleate were chosen for the following reasons:

- (a) both compounds are liquid at room temperature,
- (b) both compounds are distillable molecularly at favourable temperatures,
- (c) the great difference in refractive index permits an easy and accurate analysis of binary mixtures,
- (d) interestification during distillation is not possible, both compounds being esters from the same acid.

Methyl oleate was prepared by esterification of oleic acid with excess methanol, using sulfuric acid as a catalyst. The ester was fractionated and the fraction 146.0-147.5° C/0.5 mm Hg was used. Its constants were: n_D^{20} : 1.4520; d_4^{20} : 0.8731; r_D^{20} (specific refraction according to Lorentz-Lorenz): 0.3090.

Benzyl oleate was prepared by esterification of oleic acid with benzyl alcohol in boiling xylene with sulfuric acid as a catalyst. The water formed during the reaction was removed continuously. The ester was fractionated and the fraction 199.5-200.5° C/0.5 mm Hg was used. Its constants were: n_D^{20} : 1.4969; d_4^{20} : 0.9386; r_D^{20} : 0.3117.

The refractive index determined for mixtures of varying composition is given in Table II.

TABLE II
MIXTURES OF METHYL OLEATE AND BENZYL OLEATE

mole % methyl oleate	n_D^{20}
100.0	1.4520
91.5	1.4567
77.9	1.4636
66.2	1.4692
55.6	1.4744
37.2	1.4825
13.7	1.4918
0.0	1.4969

The results of the distillation are summarized in Table III and are shown graphically in Fig. 3.

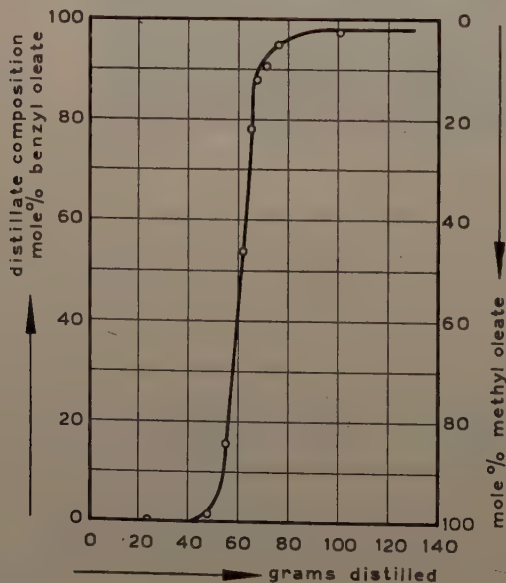


Fig. 3. Distillation curve of a methyl oleate-benzyl oleate mixture.

As will be seen, the distillation curve is of the same type as encountered in ordinary batch distillations. A good separation has been achieved as methyl oleate of at least 99% purity and benzyl oleate of 97.5% purity could be isolated.

TABLE III

DISTILLATION OF A METHYL OLEATE — BENZYL OLEATE MIXTURE

Still charge: 126.6 g. Temp.: 85-135° C (measured at the outside of the heating surface). Pressure: $5 \cdot 10^{-4}$ mm Hg. Reflux ratio: 7.5: 1. Take-off rate: 15 ml/h

Grams distilled	n_D^{20}	Mole % methyl oleate in distillate
23.3	1.4520	100.0
48.0	1.4531	98.5
54.8	1.4604	84.5
61.9	1.4786	46.0
65.2	1.4888	22.0
67.2	1.4925	12.0
71.4	1.4934	9.5
75.9	1.4950	5.0
101.3	1.4960	2.5

Styrenization of methyl esters of linseed oil fatty acids

The mixed esters of linseed oil, prepared by saponification of linseed oil and esterification of the fatty acids with excess methanol (using sulfuric acid as a catalyst) were distilled at 150-161° C/0.5 mm Hg to yield a colourless product having the following constants: n_D^{20} : 1.4633; d_4^{20} : 0.8892; ν_D^{20} : 0.3100; saponification value: 194.1 iodine value (Wijs' method): 183.

The styrenization was carried out with gaseous styrene in a glass column packed with Raschig rings according to BOELHOUWER, TJOA SOE TJOAN AND WATERMAN⁴. 170 ml esters were styrenated batchwise under the following conditions:

Temperature of column, styrene inlet and nitrogen inlet: 280° C

Styrene addition rate: 40 g/h Nitrogen rate: 1.5 l/h

Reaction time: $5\frac{1}{2}$ h.

Before and after the addition of styrene the esters were kept at 280° C for 20 minutes while 6 l/h of nitrogen were passed through the product to remove volatile matter.

After cooling to room temperature in an atmosphere of nitrogen the clear, light yellow product had the following constants: n_D^{20} : 1.5110; d_4^{20} : 0.9680; ν_D^{20} : 0.3095; S.V.: 135.4; Wt. % styrene (calculated from sap. value): 30.3.

Molecular distillation of styrenated esters

The results of the distillation are summarized in Table IV.

As the static holdup of the still was considerable (due to the high viscosity) this material was recovered by refluxing benzene in the still at atmospheric pressure several times. The benzene was removed by distillation; the product was freed from last traces of solvent under vacuum at 150° C.

The distillation losses amounted to 1.9 g (1.2% of still charge). The total styrene content of the fractions is 47.5 g while 48.2 g styrene was originally present.

All products were clear oils with gradually increasing viscosity.

DISCUSSION OF THE RESULTS

Contrary to the distillation of PETIT AND FOURNIER no cracking of the products was observed, thus the styrene content may be calculated from the saponification values. The reliability of this method is illustrated by the good agreement between total styrene content before and after distillation.

From Table IV it will be seen that a striking parallelism exists between refractive index, density, saponification value, styrene content, equivalent weight and colour. This is also brought out graphically for the refractive index and saponification value

TABLE IV

DISTILLATION OF STYRENATED ESTERS

Still charge: 150.0 g. Pressure: $1.5 \cdot 10^{-4}$ mm Hg. Reflux ratio: 7.5:1. Take-off rate: 15 ml/h at the beginning, 2 ml/h at the end of the distillation.

Fraction no.	Weight g	Temp. °C a)	Colour b)	n_D^{20}	d_4^{20}	r_D^{20}	S.F.	Wt% styrene c)	Mole styrene per mole ester	Equivalent weight	Average mol. weight d)	Weight of styrene in fraction g
1	1.27	120	SY	1.4882	0.9211	0.3129	143.5	25.2	1.0	391	—	0.32
2	1.48	—	SY	1.4823	0.9121	0.3127	150.0	21.8	0.8	374	—	0.32
3	2.24	—	W	1.4678	0.8980	0.3095	180.0	6.2	0.2	312	—	0.14
4	5.41	—	W	1.4637	0.8928	0.3089	187.1	2.5	0.1	300	—	0.13
5	7.55	—	W	1.4622	0.8967	0.3067	191.5	0.2	0.0	293	295	0.01
6	6.67	—	W	1.4626	0.9003	0.3057	188.7	1.6	0.0	297	—	0.11
7	5.80	—	W	1.4726	0.9023	0.3107	176.3	8.1	0.2	318	—	0.47
8	6.23	—	SY	1.4948	0.9330	0.3124	141.4	26.3	1.0	397	320	1.64
9	4.91	157	SY	1.4943	0.9389	0.3103	144.0	24.9	0.9	390	—	1.22
10	4.87	—	W	1.4687	0.9039	0.3080	175.2	8.7	0.3	320	—	0.42
11	5.47	—	W	1.4633	0.8927	0.3087	188.6	1.7	0.0	298	298	0.09
12	4.51	—	W	1.4740	0.9162	0.3067	172.9	9.9	0.3	325	—	0.45
13	4.78	—	SY	1.4972	0.9448	0.3098	140.5	26.7	1.0	400	—	1.28
14	7.95	—	SY	1.5078	0.9589	0.3108	133.4	30.4	1.2	420	—	2.42
15	7.11	—	LY	1.5230	0.9839	0.3105	118.6	38.2	1.7	474	429	2.72
16	6.00	192	LY	1.5231	0.9841	0.3105	120.0	37.4	1.7	467	—	2.24
17	3.05	—	LY	1.5206	0.9802	0.3104	119.2	37.8	1.7	471	—	1.15
18	2.91	—	LY	1.5258	0.9910	0.3096	117.0	39.0	1.8	480	—	1.13
19	3.83	—	LY	1.5300	0.9982	0.3095	117.1	38.9	1.8	480	—	1.49
20	4.50	—	LY	1.5293	0.9989	0.3089	117.4	38.8	1.8	478	—	1.75
21	1.64	210	LY	1.5287	1.0090	0.3056	120.3	37.3	1.7	467	—	0.61
22	2.72	—	LY	1.5274	1.0031	0.3067	122.0	36.4	1.6	460	—	0.99
23	2.94	—	LY	1.5310	1.0086	0.3068	118.9	38.0	1.7	472	—	1.12
24	2.94	—	LY	1.5341	1.0095	0.3079	114.9	40.1	1.9	489	—	1.18
25	3.31	—	LY	1.5360	1.0148	0.3073	113.9	40.6	1.9	493	670	1.34
26	2.14	—	LY	1.5377	1.0182	0.3070	114.5	40.3	1.9	490	—	0.86
27	1.86	254	LY	1.5380	1.0207	0.3064	112.9	41.1	2.0	497	—	0.76
Residue	43.0	—	YB	1.5475	1.0328	0.3073	97.6	49.1	2.7	575	—	21.1
Total 157.1												47.5

Notes:

a) measured at the outside of the heating surface.

b) SY = slightly yellow, almost white

W = water-white

LY = light yellow

YB = yellowish brown.

c) calculated from:

$$\text{wt. \% styrene} = \frac{191.8 - \text{S.V.}}{191.8} 100\%$$

191.8 being the theoretical sap. value for methyl linolenate.

d) ebullioscopically in benzene.

in Fig. 4. From the rather sharp breaks in the curve the conclusion may be drawn that a good separation has been achieved.

Fractions 4, 5, 6 and 11 clearly represent unstyrenated monomeric esters. The equivalent and molecular weights found agree closely with those calculated for methyl esters of C18 fatty acids (296.5, 294.5 and 292.5 for methyl oleate, linoleate and linolenate respectively). The specific refraction however, is lower than in the case of the original esters. This may be ascribed to a certain degree of isomerization.

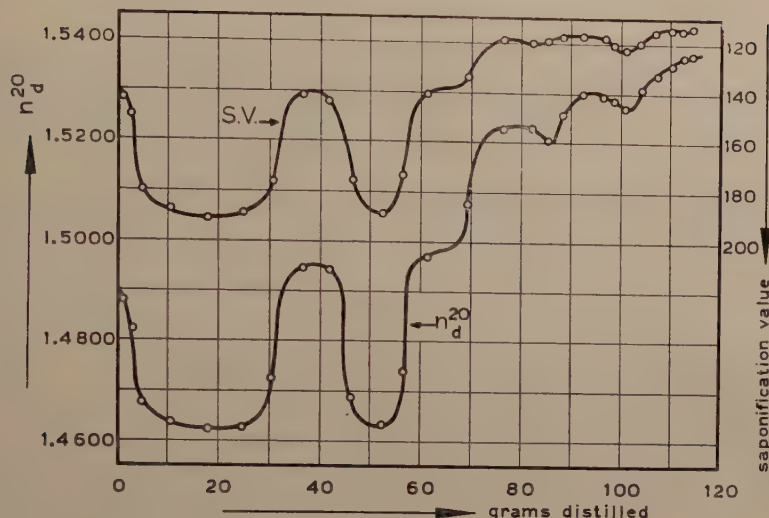


Fig. 4. Distillation of styrenated methyl esters of linseed oil fatty acids.

Though fractions 1, 2, 8 and 9 contain about one mole styrene per fatty acid chain, these products are not to be regarded as pure addition compounds of styrene and ester, since their molecular weights are obviously too low (calc. mol. wt. for mono-styrenated ester: *ca.* 398). Therefore, it seems probable that these fractions contain low molecular weight polymers of styrene (dimer and trimer).

From fraction 13 on, all products contain considerable amounts of styrene. As their specific refractions are low notwithstanding the high styrene content (values of 0.3492 and 0.3499 have been reported⁵ for the spec. refraction of monomeric styrene at 20° C), either the styrene must have polymerized to a very high degree or it must have combined chemically with the fatty acid esters. We may reject the first assumption as the products contain no products of very high molecular weight. Moreover, we calculated specific refractions for mixtures of completely dimerized esters (assuming dimerization by diene reaction) and polystyrene of infinite molecular weight and found that from fraction 15 on the experimental specific refractions are well below those calculated. We must conclude therefore, that we are dealing with compounds rather than mixtures of esters and styrene polymers.

No attempt was made to identify individual compounds. Instead, the reaction with styrene will be carried out with pure fatty acids as this will result in a less complex product.

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SUMMARY

The distillation of the reaction product of methyl esters of linseed oil fatty acids and gaseous styrene at 280° C in a highly efficient molecular still is described. From the specific refractions of the fractions obtained it follows that styrene has combined chemically with the esters.

RÉSUMÉ

La distillation du produit de réaction des esters méthyliques des acides gras de l'huile de lin et du styrène gazeux à 280° C est décrite. D'après les réfractions spécifiques des fractions obtenues, l'on peut conclure que le styrène s'est combiné chimiquement aux esters.

ZUSAMMENFASSUNG

Die Destillation des Reaktionsproduktes der Methylester der Leinöl-Fettsäuren, und des gasförmigen Styrols bei 280° C wird beschrieben. An Hand der spezifischen Refraktionen der erhaltenen Fraktionen kann man schliessen, dass das Styrol chemisch mit den Estern verbunden ist.

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THE USE OF OXINE IN THE ANALYSIS OF COMMERCIAL ALUMINIUM SULPHATE — A STATISTICAL APPROACH

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INTRODUCTION

It happens, all too often, that analyses directly following methods given in the literature give inaccurate results. Frequently, the method has been cursorily investigated, general conclusions being reached on very particular evidence or on inadequate data. On the other hand, the basis of the method is often good, and it is therefore only necessary to investigate factors (some of them by no means obvious) that have been neglected by the author. In cases where factors have been investigated, this has been done by varying them one at a time, a method which may be termed the "classical" approach. A more convenient, more revealing and less time consuming approach is that adopted in the present investigation. It is based on the familiar factorial experiment, examples of which have been given by Box¹.

The above remarks can be applied to the determination of aluminium using oxine. For some time we have experienced difficulty in the accurate determination of aluminium and iron in commercial aluminium sulphate by precipitation as the hydroxides followed by ignition to oxides. It was therefore desired to replace this method by the widely advocated oxine method. When the latter was tried, however, following procedures recommended in the literature, low and often erratic results were obtained.

The commercial aluminium sulphate to be analysed contained about 9.1% aluminium and 0.35% of iron (both ferrous and ferric). The proportion of other metals did not exceed 0.1% mainly as manganese and magnesium with traces of titanium, and were found not to interfere in the determination. It was desired to precipitate aluminium and iron oxinates together and to determine iron on a separate portion of the sample. This was considered to be the simplest procedure, since, although methods for their separation and determination as oxinates have been suggested^{2,3}, a method for the analysis of iron which is more rapid than the gravimetric oxine method has been developed in our laboratories⁴. It will be appreciated that, provided the mixed oxinate determination is accurate, slight errors in the determination of iron would be unimportant, since the proportion of the latter is small. For this reason also, preliminary experiments were concerned with determinations of aluminium alone; the effect of the presence of iron was investigated later.

EXPERIMENTAL

In the preliminary experiments, MOYER AND REMINGTON's procedure³ for the precipitation of iron and aluminium oxinates together was tested and found to give erratic results. Slightly better, but low, results were obtained using KOLTHOFF AND SANDELL's method⁵, and further investigation was based on this simpler procedure. It involves the addition of oxine to an acidic aluminium solution, heating to about 60° C, and precipitation by the slow addition of an excess of 2N ammonium acetate.

A useful review on the determination of aluminium by oxine has appeared in a paper by MILLER AND CHALMERS⁶, who were primarily interested in a micro-method. According to these authors the factors of importance in the analysis are the rate of addition of ammonium acetate and the excess of oxine used. Too great a rate of addition of acetate caused significant positive errors, and when the acetate was added very slowly, with constant (magnetic) stirring, the precision was greatly improved. A major feature of MILLER AND CHALMERS' experiments was a roughly linear relationship between the weight of excess oxine used and the percentage error in the weight of the precipitate.

Determinations following the principles of KOLTHOFF AND SANDELL⁵ and the recommendations of MILLER AND CHALMERS⁶ were carried out. Aliquots of acidic solutions of aluminium made from 99.95 + % aluminium wire were used. Ammonium acetate was added dropwise while the solutions were stirred on a bank of magnetic stirrers capable of handling six beakers at a time. The glass-enclosed iron stirrers were weighed prior to the determination and, during filtration, were allowed to fall into the sintered glass crucibles with the precipitate. The results obtained were as follows:

Number of determinations:	12
Mean weight of precipitate:	0.4351 g (Theory 0.4367 g)
Standard deviation:	0.0006 g

While these results are consistent, they are low and it was therefore decided to design a factorial experiment to ascertain the relative importance of the sources of error. The experiment was constituted as described below, the factors considered being:

- A) the volume of water used to dilute the aliquot of aluminium solution (V_{H_2O});
- B) the volume of excess oxine solution used (V_{ox});
- C) the temperature to which the solution was heated before precipitation ($T_1^\circ\text{C}$);
- D) the volume of excess ammonium acetate used (V_{ac});
- E) the volume of solution used to wash the precipitates (V_{wash});

(A 1% ammonium acetate solution was used for washing, as it was considered that the precipitates would be less liable to peptization in ammonium acetate solution than in water).

- F) the temperature of drying of the precipitates ($T_2^\circ\text{C}$);

other factors were kept constant as will be apparent.

A weighed stirrer was inserted in a beaker, 20 ml of an acidic aluminium solution (1.5219 g Al/l) pipetted in, and this diluted with V_{H_2O} ml of water. The oxine was added in an excess of V_{ox} ml, and the solution was heated to $T_1^\circ\text{C}$, determined with a thermometer. The magnetic stirrer was switched on, the thermometer rapidly rinsed with a small quantity of water, and 2N ammonium acetate run in at the rate of 2 ml/min until precipitation started, followed by a further V_{ac} ml at the same rate. Stirring was then stopped, the precipitate allowed to stand for 1-2 h and filtered off on a sintered glass crucible using a total of V_{wash} ml of 1% ammonium acetate

TABLE I FACT

V_{H_2O} (ml)		25					
V_{ox} (ml)		5.5					
T_1 ($^\circ\text{C}$)		40		60		40	
V_{ac} (ml)		50	75	50	75	50	75
$V_{wash}=200$ ml	$T_2 = 110^\circ\text{C}$	0.5254*	0.5264*	0.5265*	0.5210	0.5204	0.5210
	$T_2 = 140^\circ\text{C}$	0.5199	0.5197	0.5175	0.5182	0.5197	0.5197
$V_{wash}=300$ ml	$T_2 = 110^\circ\text{C}$	0.5223	0.5260*	0.5253*	0.5196	0.5194	0.5210
	$T_2 = 140^\circ\text{C}$	0.5181	0.5173	0.5172	0.5177	0.5188	0.5188
Weights of ox							

* These precipitates were left in a desiccator for an excessive time and formed a dark yellow

solution. The precipitates were finally dried for 1 h at $T_2^{\circ}\text{C}$, cooled for $\frac{1}{2}$ h in a desiccator, allowed to stand in the balance for 10 minutes and then weighed. The oven-drying and weighing were repeated until the weight was constant.

The results are shown in Table I, the theoretical weight of precipitate being 518.5 mg. As shown in the table, some of the results recorded are invalidated, because the precipitates were inadvertently left in a desiccator for an excessive time and formed a dark yellow crust on the surface. It will be noted that these results are unusually high.

A statistical analysis was carried out with the invalid results replaced by fictitious values to preserve the symmetry of the calculation. These fictitious values were computed in such a way as to leave the mean value of the observations (0.5193 g) unaltered and to keep the residual variance computed from all interaction terms at a minimum. The overall standard error of the observations, taking all sources of variation into account was estimated at 1.44 mg.

The effects of the main factors are given below. With one exception, there were no significant first order interactions. The 95% confidence range for any one effect was found to be ± 0.44 mg.

- A) The volume of water used to dilute the aluminium solution did not effect the results.
- B) A change in excess of 2% oxine from 5.5 ml to 15.5 ml resulted in a significant mean increase of 0.71 mg in the weight of the precipitate.
- C) Increase in the temperature of the solution before precipitation from 40° to 60° C caused the weight of the precipitates to drop by 1.23 mg, a significant amount.
- D) A change in the volume of 2N ammonium acetate from 50 to 75 ml did not affect the results. A 50 ml excess was therefore sufficient.
- E) Increase in the volume of wash solution from 200 to 300 ml resulted in a significant mean decrease of 0.50 mg in the weight of precipitate obtained.
- F) The temperature of drying was by far the most important factor, resulting in a decrease of 1.62 mg when the temperature was raised from 110° C to 140° C. It was not very practical, however, to dry at 110° C, since at this temperature the time required for the precipitate to attain constant weight was found to be excessive and the results obtained were high. In contrast, drying at 140° C was rapid and the mean of all results obtained at this temperature agreed almost exactly with the theoretical. Generally a temperature of 110° C is entirely adequate for drying a precipitate. In this case, however, it was found that there was a significant interaction between the excess of oxine used and the drying temperature, and it is possible that the process occurring in the oven was not a simple removal of excess water. This interaction was examined in a later factorial experiment.

In view of the element of doubt introduced by the faulty observations mentioned previously (all of which were from drying at 110° C) and because of the error involved in drying at 110° C, a statistical analysis was carried out on the results obtained from drying at 140° C only. The significant effects of the main factors are listed below, no first order interaction being found to be significant.

- B) Increase in the excess of oxine from 5.5 to 15.5 ml resulted in a mean increase in the weight of precipitate of 1.49 mg.
- C) Increase in the temperature of the solution before precipitation from 40° C to 60° C caused a mean decrease of 1.13 mg.

ENT ON ALUMINIUM

75									
5.5					15.5				
60		40			60			40	
75		50		75	50		75	50	
0.5207	0.5212	0.5231	0.5185	0.5191	0.5213	0.5206	0.5184	0.5187	
0.5185	0.5180	0.5187	0.5169	0.5158	0.5209	0.5198	0.5195	0.5194	
0.5184	0.5211	0.5197	0.5187	0.5179	0.5212	0.5188	0.5207	0.5201	
0.5182	0.5176	0.5172	0.5169	0.5174	0.5198	0.5196	0.5188	0.5184	

tate in g

surface.

E) Increase in the volume of solution used to wash the precipitates from 200 to 300 ml caused a mean decrease of 0.63 mg.

These conclusions are generally the same as were obtained when all the results were considered.

It should be mentioned that the increases and decreases in the weight of precipitate, caused by changes in the levels of the various factors, do not necessarily cancel each other out. The essential point of the factorial experiment was that it indicated which factors had to be controlled and how closely the control had to be effected.

In planning the second factorial experiment, designed primarily with a view to investigating the effect of iron and the interaction between the excess of oxine and the drying temperature, the levels of the non-significant factors already investigated were chosen arbitrarily. Thus the volume of water used to dilute the solution was 50 ml, the temperature of the solution before precipitation was 60° C, the excess of 2N ammonium acetate used was 50 ml and the volume of solution used to wash the precipitates was 250 ml.

The concentration of the aluminium solution used was 1.3283 g Al/l, and that of the iron 0.1000 g Fe/l. The experiment was carried out in the same way as the previous one, using 20 ml aliquots of aluminium solution and either 10 or 20 ml of iron solution. The theoretical weight of combined oxine precipitates was therefore either 0.4611 or 0.4698 g. To the solution of aluminium and iron was added 50 ml of water and 5 ml of 10% nitric acid and the solution was boiled for 1 minute (Such an oxidation with nitric acid would be necessary in the case of commercial aluminium sulphate and was found to be without effect on the determination). The solution was cooled to about 60° C, and the oxine added, the two levels of excess being again about 5.5 and 15.5 ml. The procedure was then the same as before except that the drying temperatures chosen were 120, 130 and 140° C.

If, as an approximation, a linear dependence of the weight of oxinate precipitate upon V_{ox} , T_1 and V_{wash} is assumed, the above choice of $T_1 = 60^\circ \text{C}$ and $V_{wash} = 250 \text{ ml}$ should give a mean precipitate weight in close agreement with the theoretical when the total volume of oxine is 37.5 ml ($V_{ox} = 15.5 \text{ ml}$) but a low result when $V_{ox} = 5.5 \text{ ml}$. This conclusion is based on the results of the first factorial experiment and is borne out by the determinations which are recorded in Table II. The weights of precipitates obtained with the higher excess of oxine are extremely satisfactory.

TABLE II

FACTORIAL EXPERIMENT ON THE DETERMINATION OF ALUMINIUM AND IRON TOGETHER

V_{Fe} ml	10						20					
V_{ox} ml	5.5			15.5			5.5			15.5		
$T^{\circ}\text{C}$	120	130	140	120	130	140	120	130	140	120	130	140
	0.4602	0.4599	0.4595	0.4614	0.4612	0.4601	0.4682	0.4707	0.4671	0.4698	0.4714	0.4700
	0.4600	0.4601	0.4590	0.4615	0.4611	0.4614	0.4685	0.4710	0.4684	0.4699	0.4697	0.4699
	Mean = 0.4598			Mean = 0.4611			Mean = 0.4690			Mean = 0.4701		
	Theoretical = 0.4611			Theoretical = 0.4611			Theoretical = 0.4698			Theoretical = 0.4698		
Weights of oxinate precipitate in g												

Statistical analysis showed that, as before, the excess of oxine had a profound effect on the weights of precipitate obtained. There was also a slight suggestion of an interaction between the excess of oxine and the temperature of drying, but not nearly as marked as in the first experiment. The analysis of variance suggested that the most suitable drying temperature would be 130° C, but drying took place a little more quickly at 140° C and this choice of temperature left the results correct; for further work therefore, 140° C was used.

Analysis of commercial aluminium sulphate; comparison of oxine method with other methods

In addition to the oxine method, two other methods were used for the analysis of commercial aluminium sulphate.

a) The direct ignition of the sample. For this about 2 g of aluminium sulphate were accurately weighed into a platinum crucible. After preliminary gentle heating,

the samples were finally ignited to constant weight on a blast burner at about 1300°C . The aluminium content was obtained after subtracting the iron and insoluble matter present in the sample.

b) The " R_2O_3 method". This is the usual procedure involving double precipitation of the aluminium and iron as hydroxides, followed by ignition to mixed oxides at about 1300°C . The sample is dissolved in dilute sulphuric acid and filtered before the determination.

For the oxine method the sample was also dissolved in dilute acid and filtered. Knowing the approximate composition of the sample, the optimum excess of oxine as determined in the factorial experiments was used. Other conditions of analysis were also based on the factorial experiments.

Four samples, A, B, C, D, of aluminium sulphate, with different iron contents, were used. Each sample was carefully crushed, mixed and divided into 24 portions,

TABLE III
ANALYSIS OF COMMERCIAL ALUMINIUM SULPHATE — COMPARISON OF METHODS

Method	Operator	% Al_2O_3			
		Sample A (0.48% Fe_2O_3)	Sample B (0.54% Fe_2O_3)	Sample C (0.52% Fe_2O_3)	Sample D (0.50% Fe_2O_3)
1. Oxine	I	17.04	17.34	17.43	17.41
		17.04	17.44	17.59	17.50
	II	16.95	17.30	17.54	17.40
		17.07	17.45	17.58	17.30
	III	17.10	17.36	17.57	17.43
		17.15	17.44	17.62	17.35
	IV	17.11	17.41	17.54	17.36
		17.08	17.40	17.54	17.33
	V	17.25	17.47	17.63	17.57
		17.23	17.61	17.72	17.60
	VI	17.21	17.86	17.68	17.42
		17.07	17.39	17.54	17.33
2. R_2O_3	VII	17.27	17.46	17.75	17.54
		17.26	17.41	17.72	17.54
	VIII	16.52	17.24	17.41	17.09
		17.77	17.69	17.23	17.70
Precipitation and ignition	IX	17.15	17.47	17.68	17.49
		17.13	17.50	17.63	17.50
	X	17.38	17.54	17.87	17.50
		17.34	17.52	17.95	17.43
	XI	17.24	17.63	17.85	17.60
		16.96	17.57	17.75	17.40
	XII	16.93	17.76	17.87	17.63
		17.25	17.68	17.74	17.55
3. Direct ignition	IX	17.15	17.47	17.68	17.49
		17.13	17.50	17.63	17.50
	X	17.38	17.54	17.87	17.50
		17.34	17.52	17.95	17.43
	XI	17.24	17.63	17.85	17.60
		16.96	17.57	17.75	17.40
	XII	16.93	17.76	17.87	17.63
		17.25	17.68	17.74	17.55

giving 96 portions in all. Each of the three methods was carried out in duplicate by four different operators, none of whom knew that any of the portions were the same. The order of the experiments was random. None of the operators was experienced in the direct ignition method. Of the four operators each carrying out the oxine and R_2O_3 methods, two were inexperienced (operators III and IV in the oxine method, and VII and VIII in the R_2O_3 method). Details of the results of the experiment are given in Table III.

The overall variation of the R_2O_3 method was considerably increased by the very discrepant observations of operator VIII. Although this fact itself is a criticism of the method, which fails all too easily in the hands of an inexperienced operator, the results of operator VIII were omitted in the statistical analysis, which led to the following conclusions:

1. The scatter of the results obtained by the R_2O_3 and ignition methods can be expected (with 95% confidence) to be between 1.4 and 2.8 times as great as that of the results by the oxine method.

(Residual variance for R_2O_3 method Residual variance for ignition method)
 (Residual variance for oxine method Residual variance for oxine method) ~ 4

2. The mean values (% Al_2O_3), their 95% confidence ranges and mean differences between results by the various methods are as follows:

Sample	Oxine Method	R_2O_3 Method	Ignition Method	Mean Differences	
	(4 operators)	(3 operators)	(4 operators)	2-1	3-1
A	17.07 ± 0.04	17.22 ± 0.10	17.17 ± 0.09	0.15	0.10
B	17.39 ± 0.04	17.53 ± 0.10	17.58 ± 0.09	0.14	0.19
C	17.55 ± 0.04	17.67 ± 0.10	17.79 ± 0.09	0.12	0.24
D	17.39 ± 0.04	17.50 ± 0.10	17.51 ± 0.09	0.11	0.12

The least significant difference (95% confidence) between an R_2O_3 and an oxine determination was found to be 0.11, and that between an ignition and an oxine determination 0.095. The above mean differences are therefore all significant.

3. The 95% confidence ranges for a single observation by the three methods are: Oxine ± 0.112 ; $R_2O_3 \pm 0.242$; Ignition ± 0.240 .

DISCUSSION

The consistent and accurate results obtained by the oxine method in the second factorial experiment and in the analyses of aluminium sulphate can generally be attributed to a rigid adherence to the chosen experimental conditions. It was considered that one of the important factors, and a probable main cause of erratic results obtained in the preliminary experiments, was the method of stirring. While consistent results may sometimes be obtained with hand stirring, there would always be an element of doubt attached to the procedure. The usual mechanical stirring was rejected because the precipitate adheres to the stirrer and its removal is often difficult.

The difference in the consistency between the results obtained with the oxine method on the one hand and those of the R_2O_3 and ignition methods on the other is striking. The reason for the discrepancy was not, however, investigated. The R_2O_3 method is comparatively tedious and the errors have been discussed at length in the literature⁷. While the direct ignition method is rapid, it also has the disadvantage associated with ignitions of alumina, and probably has other sources of error as well.

RECOMMENDED PROCEDURE

For analyses of aluminium or aluminium and iron in solutions containing the equivalent of about 30 mg of aluminium per determination, the following procedure will give good results:

Pipette a suitable aliquot of the solution into a beaker containing a weighed magnetic stirrer bar. If required, oxidize the iron by boiling with 5 ml of 10% nitric acid. Cool to about 40° C, add a 15.5 ml excess of 2% oxine in *N* acetic acid solution and heat to 63° C. Place the beaker on the magnetic stirrer and switch this on. When the temperature has dropped to 60° C, add 2*N* ammonium acetate at the rate of 2 ml/min until precipitation starts and then a further 50 ml at the same rate. Allow the precipitate to stand for about 1 h and filter through a number 4 porosity sintered glass crucible, carefully allowing the stirrer to enter the crucible with the precipitate. Use a total of 250 ml of 1% ammonium acetate for both removing the precipitate from the beaker and washing it on the crucible. Do not allow the crucible to suck dry until filtration is complete. Dry the precipitate at 140° C, cool in a desiccator for $\frac{1}{2}$ h, place in the balance case for 10 min and weigh. Repeat to constant weight.

ACKNOWLEDGEMENTS

The author wishes to express his grateful thanks to the following: Dr. H. A. E. MACKENZIE and Dr. H. L. DAVIES for continual advice and guidance; Mr. D. C. GOCH for the design and analysis of the factorial experiments and for his advice on all statistical aspects of the problem; Experimental Officers of the Research Department, particularly Miss Y. BOTHA and Mr. H. W. BERGH for their painstaking analyses; Messrs. AFRICAN EXPLOSIVES and CHEMICAL INDUSTRIES, LTD., for their permission to publish this paper.

SUMMARY

The analysis of commercial aluminium sulphate by precipitation of the aluminium and iron with 8-hydroxyquinoline (oxine) has been investigated. Factorial experiments were used to determine what control of experimental conditions was required for accurate results. The oxine method was compared with other methods and found to be considerably more accurate and precise, provided that correct conditions of precipitation were rigidly adhered to.

RÉSUMÉ

L'analyse du sulfate d'aluminium par précipitation de l'aluminium et du fer au moyen de la 8-hydroxyquinoléine (oxine) a été examinée. Des essais factoriels ont été effectués pour déterminer les conditions expérimentales permettant d'obtenir des résultats exacts. Après comparaison avec d'autres méthodes, on arrive à la conclusion que l'analyse au moyen de l'oxine est la plus exacte et la plus précise, si l'on suit rigoureusement les conditions données pour la précipitation.

ZUSAMMENFASSUNG

Die Analyse von technischem Aluminiumsulfat wurde durch Fällung von Aluminium und Eisen mit 8-Hydroxychinolin (Oxin) ausgeführt. Durch faktorielle Experimente wurde festgestellt, welche Versuchsbedingungen genau beachtet werden müssen, um richtige Ergebnisse zu erlangen.

Die Oxin-Methode wurde mit anderen Methoden verglichen und als wesentlich genauer und richtiger als diese befunden — immer vorausgesetzt, dass die Fällungsbedingungen richtig eingehalten werden.

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CONTRIBUTION À L'ÉTUDE DE LA SÉPARATION DES TERRES RARES DE FISSION PAR L'ACIDE ÉTHYLÈNEDIAMINETÉTRAACÉTIQUE

par

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Laboratoire de Chimie Analytique, Université de Liège (Belgique)

Les très grandes différences dans la stabilité des complexes des terres rares avec l'acide éthylènediaminetétraacétique, ont amené les chercheurs à étudier, depuis quelque temps, la séparation de ces terres rares en présence de ce complexant sur résine cationique.

A côté de chercheurs qui se sont attachés à étudier la séparation de terres rares dans un but de chimie préparative, MAYER ET FREILING¹, notamment, ont déterminé les conditions de séparation des mélanges Y-Tb-Eu-Sm pour des quantités de l'ordre de quelques mg: ils ont conclu à l'efficiencia particulière de l'EDTA par rapport aux autres complexants.

Le Laboratoire de Radiochimie de l'Université de Liège étudie, depuis bientôt 2 ans, l'utilisation de l'EDTA pour la séparation chromatographique des produits de fission de l'uranium**, et, en particulier, la séparation de terres rares.

Voici quelques résultats obtenus dans la séparation des éléments de longue vie; les terres rares employées sont d'abord séparées chimiquement des autres produits de fission selon le procédé décrit dans CORVELL ET SUGARMANN².

1. Séparation ^{61}Y - ^{147}Pm - ^{144}Ce (4 mg Y_2O_3 — Pm carrier free — Ce^{+3} : max. 20 γ de CeO_2 . Mélange radioactif versé sur la résine à pH = 2.2).

La Figure 1 montre une séparation déjà excellente à pH = 3.65 (mesuré à 80° C, température de la colonne). A pH = 3.05-3.1, (Fig. 2), la séparation est quantitative; la traînée qui suit le pic de l'yttrium paraît être due à un mélange Y - ^{155}Eu , ainsi que semblent le montrer des décroissances suivies pendant quelques mois.

2. Pour résoudre ce problème, des mélanges synthétiques ^{61}Y - ^{152}Eu ont été réalisés et des séparations entreprises (2 mg Y_2O_3 -60 γ Eu_2O_3 -versés à pH = 2.2 sur la résine).

Ainsi que le montrent les Figures 3 et 4, la séparation, quasi nulle à pH = 3.5, devient presque quantitative à pH = 3.05-3.1. La traînée de la Figure 2 qui n'est observée que lorsqu'on descend à pH 3.1 paraît donc être due à l' ^{155}Eu , très malaisé à mettre en évidence dans les produits de fission à cause de sa très faible teneur (0.02 à 0.03%) et de son rayonnement très peu pénétrant. Il est à noter comme argument supplémentaire que cette traînée s'observe au même endroit dans la séparation ^{61}Y - ^{152}Eu à pH = 3.05.

* Chercheur agréé à l'Institut Interuniversitaire des Sciences Nucléaires.

** Il nous est agréable de remercier M. HUBERT, Directeur au CEA FN qui a bien voulu mettre à notre disposition de l'U irradié ainsi que les radioisotopes nécessaires à cette recherche.

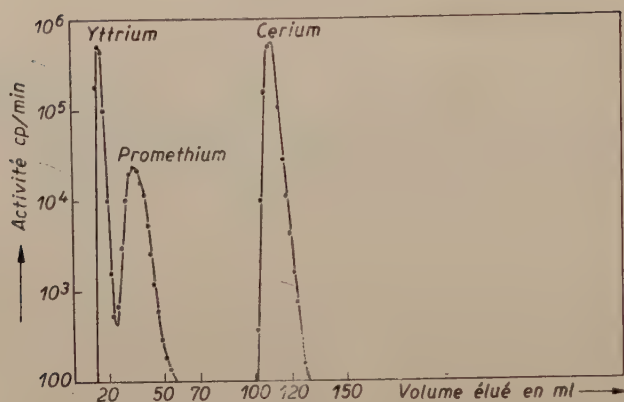


Fig. 1.

Dowex 50: 74-36 μ
 Complexon II: $2.5 \cdot 10^{-2} M$
 pH: 3.65 ± 0.05
 T: $80^\circ C$
 Résine NH_4 : 12 g 53

Hauteur de colonne: 34.6 cm
 Section: 1 cm^2
 Volume libre: 12.15 ml
 Vitesse d'élution: 0.88 $ml/cm^2/min$

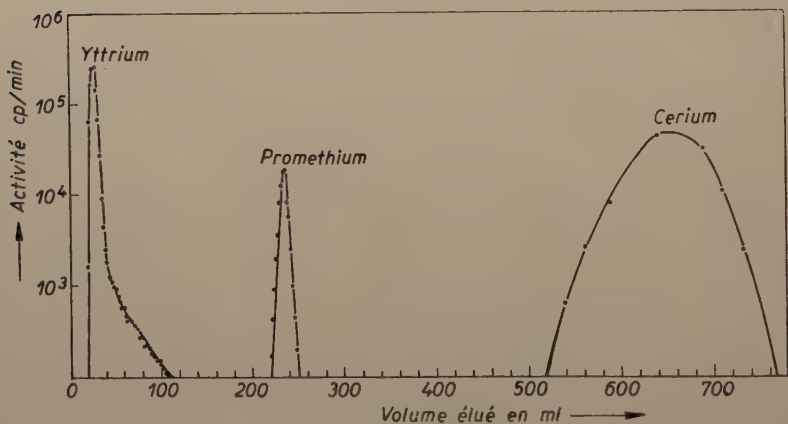


Fig. 2.

Dowex 50: 74-36 μ
 Complexon II: $2.5 \cdot 10^{-2} M$
 pH: 3.05-3.1
 T: $80^\circ C$
 Résine NH_4 : 12 g 49

Hauteur de colonne: 35 cm
 Section: 1 cm^2
 Volume libre: 12.60 ml
 Vitesse d'élution: 0.94 $ml/cm^2/min$

3. Cependant, les séparations à pH = 3.05 avec le complexon $2.5 \cdot 10^{-2} M$ sont malaisées; car la solution éluante est sursaturée à froid et elle finit par cristalliser au sortir de la colonne lorsque l'opération se prolonge. Une élution du mélange ^{61}Y - ^{152}Eu - ^{147}Pm - ^{144}Ce à pH = 3.15-3.2, toutes autres conditions égales, ne présente pas ces inconvénients mais la séparation est beaucoup moins bonne ainsi que le montre la Figure 5.

Il est à remarquer, cependant, que dans cette séparation, les 2 pics-Y et Eu sont très raides et qu'entre eux, on constate un facteur de décontamination supérieur à 10, c'est-à-dire que les points maxima présentent une très grande pureté.

4. Une séparation Y-Eu-Pm-Ce a été de nouveau réalisée, directement cette fois sur le mélange de fission et dans des conditions expérimentales meilleures que celles de la séparation indiquée par la Figure 2. Dans cette séparation, on constate effectivement la présence du pic de l' ^{155}Eu ,

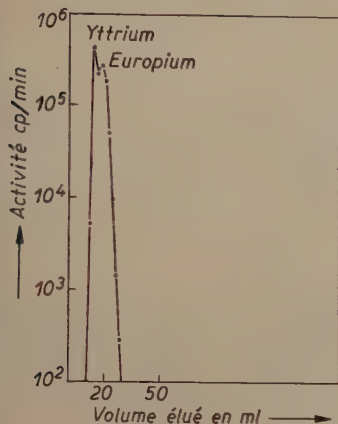


Fig. 3.

Dowex 50: 74-36 μ
 Complexon II: $2.5 \cdot 10^{-2} M$
 pH: 3.5
 T: 80°C
 Résine NH_4 : 12 g 49
 Hauteur de colonne: 33.4 cm
 Section: 1 cm²
 Volume libre: 12.00 ml
 Vitesse d'élution: 0.80 ml/cm²/min

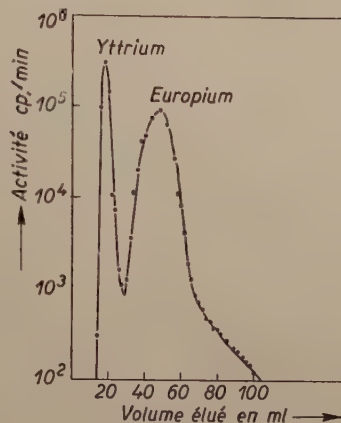


Fig. 4.

Dowex 50: 74-36 μ
 Complexon II: $2.5 \cdot 10^{-2} M$
 pH: 3.05-3.1
 T: 80°C
 Résine NH_4 : 12 g 49
 Hauteur de colonne: 33.4 cm
 Section: 1 cm²
 Volume libre: 12.00 ml
 Vitesse d'élution: 0.81 ml/cm²/min

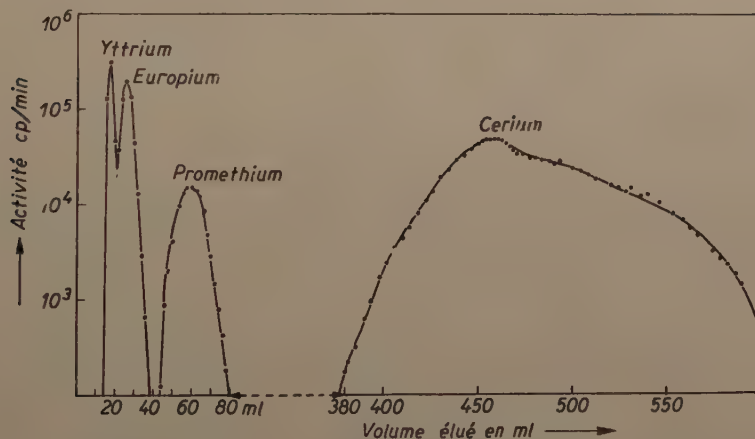


Fig. 5.

Dowex 50: 74-36 μ
 Complexon II: $2.5 \cdot 10^{-2} M$
 pH: 3.15-3.2
 T: 80°C
 Résine NH_4 : 12 g

Hauteur de colonne: 33.4-5 cm
 Section: 1 cm²
 Volume libre: 12.2 ml
 Vitesse d'élution: 0.59 ml/cm²/min

très petit (le max. du pic est à 750 c/) alors que celui de l'Y, dans cette séparation, est à 130.000 c/) mais bien séparé. Des mesures d'absorption du rayonnement dans l'Al montrent qu'il s'agit bien de ^{156}Eu . La certitude sera absolue, lorsque, pendant quelques mois encore, nous aurons suivi la décroissance de cet élément.

En conclusion, toutes autres conditions inchangées, nous proposons de travailler à $\text{pH} = 3.05$ pour éluer Y-Eu-Pm puis d'élever le pH à 3.65. Cette façon d'opérer permet de recueillir le Ce dans un volume relativement réduit.

La recherche est actuellement poursuivie moyennant diverses modifications techniques.

Il nous est agréable de remercier MM. GUEBEN et GOVAERTS pour leur précieuse collaboration, ainsi que le Directeur de l'I. I. S. N. pour les subsides qui nous ont été accordés.

RÉSUMÉ

Dans le présent article, les auteurs recherchent les conditions d'une séparation rapide et si possible analytique d'un mélange Y-Eu-Pm-Ce pour des quantités de l'ordre de quelques milligrammes.

On donne des courbes d'élution en fonction du pH, qui est le facteur d'influence prépondérant. Une séparation à pH 3.05 donne les meilleurs résultats.

SUMMARY

In the present paper, the authors investigate the conditions for a rapid and if possible analytical separation of a mixture Y-Eu-Pm-Ce for quantities of a few milligrams.

Elution curves are given in function of the pH, which is the main influencing factor.

A separation at pH 3.05 gives the best results.

ZUSAMMENFASSUNG

In diesem Artikel, untersuchen die Autoren die Bedingungen einer raschen und wenn möglich analytischen Trennung einer Mischung von Y-Eu-Pm-Ce für Mengen von wenigen Milligrammen.

Elutionskurven in Abhängigkeit vom pH, welcher der überwiegende Einflussfaktor ist, werden gegeben.

Eine Trennung bei pH 3.05 gibt die besten Ergebnisse.

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Reçu le 6 août 1955

THE DIETHYLDITHIOCARBAMATE OF MERCURY: COMPOSITION,
STRUCTURE AND ANALYTICAL APPLICATION.

A HETEROMETRIC STUDY

by

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INTRODUCTION

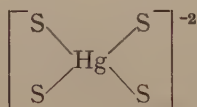
Our aim was to study the structure and composition of sulfides by the heterometric method (= photometric study of suspensions). It appeared to us that the heterometric method was most suited to this purpose. The use of alkaline sulfide solutions was excluded because they are not sufficiently stable. As compared to the latter, the sodium salt of diethyldithiocarbamate is soluble in water and the solution obtained is stable for a long time even at a $0.001M$ concentration. Mercuric carbamate was chosen for our investigation. It is insoluble in water and is colourless. It was found that the most insoluble mercuric compound which was obtained at room temperature, had the composition $Hg(CBM)_2$ (CBM = diethyldithiocarbamic anion). This compound could be obtained in acetic acid, acetate or ammoniacal solutions, in two ways: either by the heterometric titration of mercuric nitrate with $Na(CBM)$ or vice versa. In addition to $Hg(CBM)_2$, intermediate compounds also exist, but they are quantitatively transformed into $Hg(CBM)_2$. The latter proved to be insoluble in the presence of most complexing agents. Pyro- and tripolyphosphate were without influence. Neither was the compound changed in citrate or ethylenediaminetetraacetic acid solutions containing large excesses of ammonia. Our experiments showed that $Hg(CBM)_2$ is the most insoluble of the carbamates of the bivalent cations.

Very many publications have appeared recently dealing with the analytical use of carbamates, especially for the determination of copper as well as of cadmium, zinc, etc. The compounds of mercury seem to be neglected. (The literature on carbamates can be taken from recent analytical handbooks.) The different carbamates are soluble in organic solvents as CCl_4 , $CHCl_3$ and, in the case of coloured solutions, the latter are used for the quantitative photometric determination of metals at chosen wavelengths. All workers in this field have assumed that the metal carbamates obtained are *complex* compounds. Their structures have probably not been investigated although their compositions are cited as $Me^{II}(CBM)_2$, whilst those of the trivalent cations probably have the composition $Me^{III}(CBM)_3$.

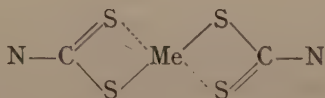
Difficulties are encountered in attempting to conceive the structure for $\text{Me}^{\text{II}}(\text{CBM})_2$. Sterically, a structure such as:



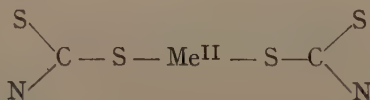
in which both the nitrogen and the sulfur, which are bound to the metal, come from the *same* carbamate, is extremely difficult to conceive. On the other hand, we know from our investigations, that ethylenediaminetetraacetate solutions containing large excesses of NH_3 have no influence on the $\text{Hg}(\text{CBM})_2$ compound. The problem is therefore, firstly, how to present a general structure for the carbamates recognizing that they are very stable covalent compounds, and secondly, to establish if and when nitrogen is involved in the structure of $\text{Me}^{\text{II}}(\text{CBM})_2$. In a previous report¹ we showed that a soluble anion complex with mercaptobenzthiazole is formed which has a structure:



With many cations CBM gives insoluble, frequently colourless, carbamates. Some amongst them have no affinity to nitrogen. It seems reasonable therefore not to include the nitrogen in the complex formation. On the other hand, if the structure is assumed to be



the same difficulties are encountered sterically. It may well be that the formation of



is already sufficient to give a covalent compound. If four sulfurs participate in the compound, then they must come from four carbamate anions, and the $\text{Me}^{\text{II}}(\text{CBM})_2$ would then have to be a dimer $(\text{Me}^{\text{II}}(\text{CBM})_2)_2$ in the most simple case. On the other hand, the affinity of mercury to nitrogen may produce bonds of another character.

On studying the heterometric curves it can be seen that traces of either mercuric mercury or of CBM may be determined heterometrically with an error which is close to zero.

EXPERIMENTAL

The heterometric method, which was developed by the first author and has already been discussed elsewhere^{2,3} was used for this study. The curves obtained were used for the determination of mercury or CBM. All titrations were carried out at 20° C. 20 ml solution was used for the titration which was carried out in a vessel with a diameter of 4 cm. All reagents used were either analytical reagents or chemically pure reagents. A few drops of nitric acid were added to the concentrated stock solution of mercuric nitrate (mercuric nitrate crystallized reagent $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, Baker and Adamson). The more dilute solutions were then obtained by diluting in water. The sodium diethyldithiocarbamate was an Eastman pure product. The solutions of NaCBM were obtained by weighing the calculated amount of the salt which was then dissolved in water.

RESULTS AND DISCUSSION

pH — Heterometric titrations

A parallel pH and heterometric titration was carried out with 20 ml solution, which had the following composition:

3 ml 0.002M $\text{Hg}(\text{NO}_3)_2$ + 4 ml 0.025M $\text{Na}_2\text{H}_2\text{-ethylenediaminetetraacetate}$ + 2 ml 0.007M sodiumdiethyldithiocarbamate + 3 ml H_2O + 2 ml 0.1N HNO_3 + 2 ml 0.1M CH_3COOH + 4 ml 0.1M NH_4NO_3 .

The solution was titrated dropwise with 0.2M NaOH. At pH \sim 2.5 a precipitate of mercuric carbamate already appeared, and the density caused by the precipitate did not change until pH \sim 11.5. A horizontal density line was obtained, showing that the precipitate is not influenced by the ethylenediaminetetraacetate whatever the pH conditions.

Titration of mercury with CBM. Fig. 1 presents the composition and the results of titrations of an aqueous mercuric nitrate solution with Na(CBM). The concentration of mercury was between $0.75 \cdot 10^{-4}\text{M}$ and $3 \cdot 10^{-4}\text{M}$ ($= 0.3012$ mg Hg/20 ml — 1.2036 mg Hg/20 ml). The titrations were carried out in acetic acid, acetate or ammoniacal solution. In all cases at the end of the titration, straight maximum optical density lines were obtained and the maximum density values rose with the increased amount of mercury added.

In each case the first maximum optical density point (which indicates the end of the reaction) was obtained exactly at the molar ratio of 1 Hg : 2 CBM. The error was 0-2%. This means that a few tenths of a milligram of mercury in 20 ml aqueous solution or one part of mercury in about 50,000 parts of water can be determined by heterometric titration with CBM, with an error which is generally close to zero. The time was 15-30 minutes.

The curves obtained are rather interesting as the existence of additional mercuric-CBM compounds could be deduced from them. Thus, analysing curve 1 it may be established that the point of the initial precipitation lies at the molar ratio of 1 Hg : 1 CBM. Both above titrations were carried out in a dilute sodium acetate solution.

When the titration was carried out in acetic acid solution (curves 5 and 6), even at different concentrations of mercury, the point of the initial precipitation in both curves is at the same molar ratio, i.e. (1 Hg : 1 CBM ?). Curve 3, which was obtained

when the titration was carried out in concentrated ammonia solution is more complicated. The last break lies at 1 Hg : 2 CBM but, in addition, another break is discernible.

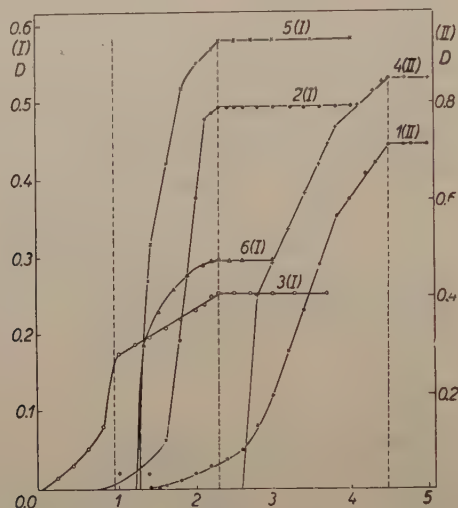


Fig. 1.

- 1) $3 \text{ Hg}(\text{NO}_3)_2$ $0.002M$ + $2 \text{ CH}_3\text{COONa}$ $0.1M$ + $15 \text{ H}_2\text{O}$ + $x \text{ D.D.C.A.}$ $0.0028M$.
Titration time 15 min.
- 2) $3 \text{ Hg}(\text{NO}_3)_2$ $0.001M$ + $2 \text{ CH}_3\text{COONa}$ $0.1M$ + $15 \text{ H}_2\text{O}$ + $x \text{ D.D.C.A.}$ $0.0028M$.
Titration time 55 min.
- 3) $3 \text{ Hg}(\text{NO}_3)_2$ $0.001M$ + 2 NH_3 $2M$ + $15 \text{ H}_2\text{O}$ + $x \text{ D.D.C.A.}$ $0.0028M$.
Titration time 25 min.
- 4) $3 \text{ Hg}(\text{NO}_3)_2$ $0.002M$ + $1 \text{ CH}_3\text{COOH}$ M + $16 \text{ H}_2\text{O}$ + $x \text{ D.D.C.A.}$ $0.0028M$.
Titration time 30 min.
- 5) $3 \text{ Hg}(\text{NO}_3)_2$ $0.001M$ + $1 \text{ CH}_3\text{COOH}$ M + $16 \text{ H}_2\text{O}$ + $x \text{ D.D.C.A.}$ $0.0028M$.
Titration time 15 min.
- 6) $3 \text{ Hg}(\text{NO}_3)_2$ $0.0005M$ + $1 \text{ CH}_3\text{COOH}$ M + $16 \text{ H}_2\text{O}$ + $x \text{ D.D.C.A.}$ $0.0014M$.
Titration time 20 min.

Titration of sodium carbamate with mercuric nitrate. The results obtained in the reverse titration of CBM with mercury are compiled in Fig. 2. The final concentration of CBM was $0.0007M$ (curves 1 and 2) and $0.00033M$ (curves 3 and 4).

Analysing the curves, the following conclusions may be drawn. The maximum optical density values of experiments 1 and 2 are the same, but the character of the curves is different: in the ammoniacal solution (curve 2) excess of mercury causes no change, but in sodium acetate solution (curve 1) the excess of mercury gradually dissolves the precipitate. Probably, $\text{Hg}(\text{CBM})_2$ is transformed into $\text{Hg}(\text{CBM})$ which is more soluble.

With lower concentrations of CBM the maximum density value in the presence of sodium acetate (curve 3) is much higher than with ammonia (curve 4). In both cases, horizontal maximum optical density lines were obtained. In all experiments, the first maximum optical density point lies at the end of the formation of $\text{Hg}(\text{CBM})_2$. The error is practically equal to zero. 0.5-1.0 mg of $\text{Na}(\text{CBM})$ which was dissolved

in 20 ml water were titrated with mercury and theoretical results were obtained. The titration time was about 40 minutes.

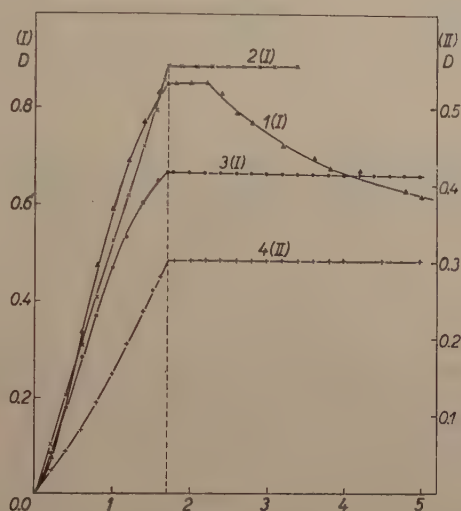


Fig. 2.

- 1) 5 D.D.C.A. $0.008M$ + 2 CH_3COONa $0.1M$ + 13 H_2O + x $Hg(NO_3)_2$ $0.004M$.
Titration time 45 min.
- 2) 5 D.D.C.A. $0.0028M$ + 2 NH_3 $2M$ + 13 H_2O + x $Hg(NO_3)_2$ $0.004M$.
Titration time 45 min.
- 3) 5 D.D.C.A. $0.0014M$ + 2 CH_3COONa $0.1M$ + 13 H_2O + x $Hg(NO_3)_2$ $0.002M$.
Titration time 40 min.
- 4) 5 D.D.C.A. $0.0014M$ + 2 NH_3 $2M$ + 13 H_2O + x $Hg(NO_3)_2$ $0.002M$.
Titration time 30 min.

CONCLUSIONS

Composition

1) Hg^{+2} when titrated heterometrically with sodium diethyldithiocarbamate (= Na(CBM)) in acetate or acetic acid solution, gives the first maximum density point exactly at the molar ratio of 1 Hg : 2 CBM.

Excesses of CBM have no influence on the compound obtained.

2) An intermediate, $Hg(CBM)$, exists; it is more soluble than $Hg(CBM)_2$ and is transformed quantitatively into the latter compound.

3) The reverse titration of CBM with Hg^{+2} , giving the insoluble $Hg(CBM)_2$, can be carried out with the same success.

Analysis

0.3-1.2 mg Hg in 20 ml aqueous solution can be titrated with Na(CBM) $0.004M$ solution.

Or vice versa, 0.5-1.0 mg Na(CBM) in 20 ml aqueous solution can be titrated with mercuric nitrate, $0.002M$ - $0.004M$. The error in both cases is mostly equal to zero. Both titrations can be carried out in acidic, alkaline or ammoniacal solutions.

SUMMARY

0.3–1.2 mg of mercury ($= \text{Hg}(\text{NO}_3)_2$) in 20 ml aqueous solution, can be titrated heterometrically with sodium diethyldithiocarbamate (NaCBM).

Vice versa, 0.5–1.0 mg NaCBM in 20 ml aqueous solution can be titrated heterometrically with mercuric nitrate.

In both cases the error is mostly equal to zero. The insoluble $\text{Hg}(\text{CBM})_2$ is obtained in both cases.

RÉSUMÉ

0.3–1.2 mg de mercure ($= \text{Hg}(\text{NO}_3)_2$) dans 20 ml de solution aqueuse peuvent être titrés hétérométriquement avec le diéthylthiocarbamate de sodium (NaCBM), ou vice-versa, 0.5–1.0 mg de NaCBM dans 20 ml de solution aqueuse peuvent être titrés hétérométriquement avec le nitrate de mercure(II).

Dans les deux cas, l'erreur est presque nulle. $\text{Hg}(\text{CBM})_2$ insoluble est obtenu dans les deux cas.

ZUSAMMENFASSUNG

0.3–1.2 mg Quecksilber ($= \text{Hg}(\text{NO}_3)_2$) in 20 ml wässriger Lösung kann man heterometrisch mit Natriumdiäthylthiocarbamat (NaCBM) titrieren. Umgekehrt kann man 0.5–1.0 mg NaCBM in 20 ml wässriger Lösung mit $\text{Hg}(\text{NO}_3)_2$ titrieren. In beiden Fällen ist der Fehler meistens gleich null und das unlösliche $\text{Hg}(\text{CBM})_2$ wird erhalten.

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DETERMINATION OF TRACE QUANTITIES OF BORON WITH TWO NEW COLORIMETRIC REAGENTS

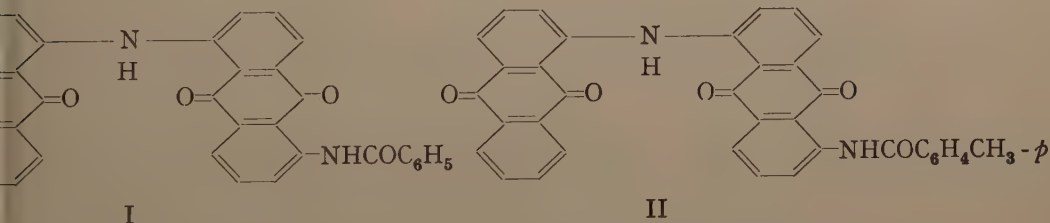
by

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INTRODUCTION

Two new colorimetric methods for the determination of minute quantities of boron have been developed. The methods are based upon the formation of stable boron complexes of 5-benzamido-6'-chloro-1,1'-bis (anthraquinonyl)amine (Compound I) and 5-*p*-toluidino-1,1'-bis(anthraquinonyl)amine (Compound II), respectively, in concentrated (96%) sulfuric acid solution.



A procedure for rapidly decomposing the sample and subsequently separating the boron, as trimethyl borate, was also developed.

The results of this study show that the new methods are useful for the colorimetric determination of boron and that they have high sensitivities (Method I, 1 part of boron in 300 million parts of solutions; Method II, 1 part of boron in 200 million parts of solution), absorbance measurements being made in 1 cm cells at 635 $m\mu$ and 720 $m\mu$, respectively.

Apparatus

All measurements were made with a Beckman spectrophotometer, Model DU, using matched 1-cm Corex cells.

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The distillation apparatus (Fig. 6) was constructed with Corning brand alkali Resistant Glass No. 7280. This brand of glassware was used because of its low boron content (maximum B_2O_3 , 0.2%). "Blanks" indicated that there is no boron contamination from this type of glassware.

Pipets and volumetric flasks were of Kimble Brand glass.

A 250-watt G.E. Infrared Heat Lamp was employed for all evaporations.

Reagents

Compound I is a dark red solid and forms a greenish-yellow solution that turns to a deep red when heated at $130^\circ C$ in 96% sulfuric acid. A $5 \cdot 10^{-3}M$ solution was prepared by dissolving 0.2910 g of reagent in 100 ml of 96% sulfuric acid. Solutions of lower concentrations were prepared by proper dilution with 96% sulfuric acid.

Compound II is also a dark red solid and forms a straw-colored solution that changes to a deep red when heated at $130^\circ C$ in 96% sulfuric acid. A $1 \cdot 10^{-3}M$ solution was prepared by dissolving 0.0534 g of reagent in 100 ml of 96% sulfuric acid. Compounds I and II may be obtained from the LaMotte Chemical Products Co., Towson, Baltimore, Md. (U.S.A.).

A standard boron solution, containing 1.00 mg of boron per ml, was prepared by dissolving 0.5736 g of reagent grade *ortho* boric acid in 96% sulfuric acid to a volume of 100 ml. Boron solutions of lower concentrations were prepared by proper dilution with 96% sulfuric acid.

Stock solutions of the diverse ions were made with reagent grade compounds dissolved in 96% sulfuric acid. Each contained 1 mg of the desired ion per ml, except solutions of Fe^{+3} , Co^{+2} , Cu^{+2} , Mn^{+2} , Mg^{+2} and Cr^{+3} ions. Saturated solutions of the latter were used.

EXPERIMENTAL

Method I

Fig. 1 shows the absorbance curves of Compound I and of its colored boron complex. All measurements were made against 96% sulfuric acid as a blank. The complex shows a maximum at $635 m\mu$. The absorbance of the reagent is very small at the wavelength of maximum absorbance ($635 m\mu$) of the complex, thus adding to the precision of the method.

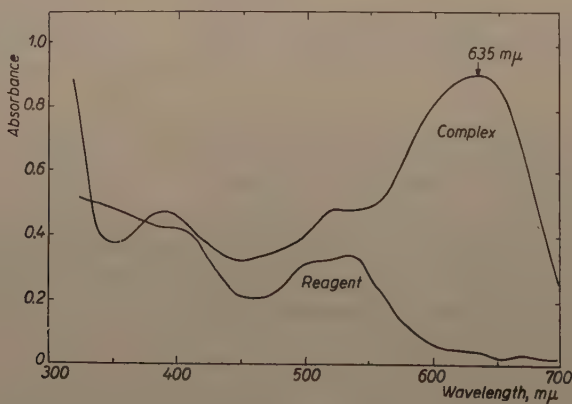


Fig. 1. Absorbance curves of Compound I and of its colored boron complex.

In order to evaluate the use of the boron complex maximum in the determination of small amounts of boron, a study of the important properties of the absorption band was made.

Effect of sulfuric acid concentration. The colored complex shows considerable decrease in absorbance as the sulfuric acid concentration is decreased. The effect of sulfuric acid concentration was determined by measuring the absorbances of solutions containing $3.0\ \mu\text{g}$ of boron, $1.0\ \text{ml}$ of reagent, heating for $1\frac{1}{2}$ hours at 130°C in an oven, and diluting to $10\ \text{ml}$ volume with varying percentages of sulfuric acid. For precise results the acid content must be at least 96% by weight.

Rate of reaction and stability of complex. Because it is necessary to heat for several hours in order to develop full color intensity, the rate study was made at three temperatures: 100° , 130° , and 150°C . The study at 100°C showed a slow rate of formation for the boron complex. At 150°C a sharp increase in absorbance is obtained after a half hour, but with prolonged heating the absorbance decreases. At 130°C a sharp increase in absorbance is noted up to $1\frac{1}{2}$ hours, after which no appreciable increase occurs. Upon standing for 59 days, the complex showed only a 3.4% increase in absorbance, a color stability quite adequate for analytical application.

The boron complex in solution. Three methods were employed to establish the empirical formula of the boron complex in solution. These were the mole ratio method of YOE AND JONES¹, the method of continuous variations introduced by JOB² and modified by VOSBURGH AND COOPER³, and the slope ratio method recently proposed by HARVEY AND MANNING^{4,5}.

In applying the mole ratio method to the boron complex, solutions were prepared so that the reagent concentration was maintained constant at $2 \cdot 10^{-4}M$ and the ratio of moles of boron to moles of reagent varied from 0.5 to 4.0. A sulfuric acid blank was used in all measurements. The results in Fig. 2 indicate a one to one ratio.

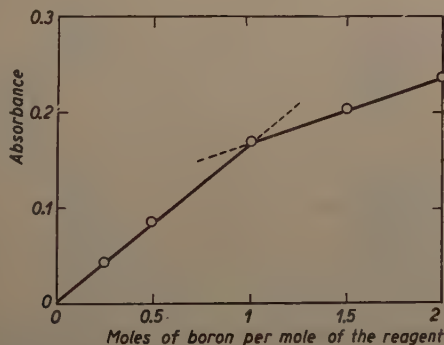


Fig. 2. Mole ratio method applied to the boron complex.

For the method of continuous variations, solutions were prepared containing $x\ \text{ml}$ of a $1 \cdot 10^{-4}M$ reagent solution and $(5-x)\ \text{ml}$ of a $1 \cdot 10^{-4}M$ boron solution. The absorbances of these solutions *versus* a sulfuric acid blank were then measured at $635\ \mu\mu$. The results are shown in Fig. 3. A maximum occurs at $x = 2.45$, so that $n = 1.04$, again indicating a reagent-to-boron ratio of 1:1.

In applying the slope ratio method, a series of solutions was prepared containing 20 γ of boron per 10 ml (an excess) and varying the concentration of the reagent. The absorbances were measured against a sulfuric acid blank. A second series was prepared $5 \cdot 10^{-4}M$ with respect to the reagent (an excess) and varying the amount of

boron. The absorbances of this series were measured against a reagent blank. The results are shown in Fig. 4. From Fig. 4 $\text{slope}_1 = 1.620$ (boron in excess) and slope_2

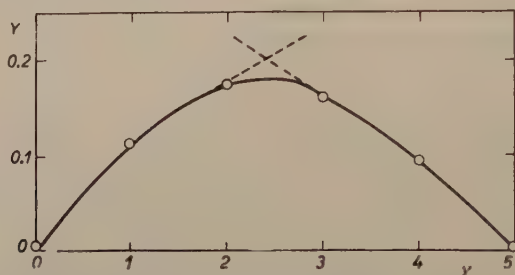


Fig. 3. Continuous variations method applied to the boron complex.

$= 1.680$ (reagent in excess). Hence the reagent-to-boron ratio is 1.03, a ratio in good agreement with the other two methods.

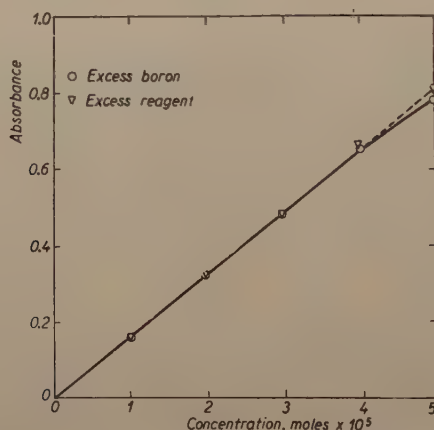
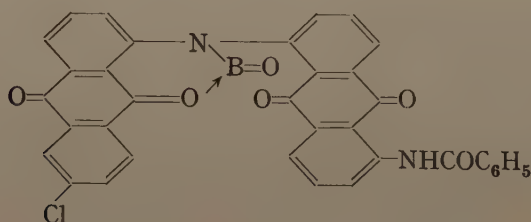


Fig. 4. Slope ratio method applied to the boron complex.

The results obtained by the three techniques indicate that one atom of boron reacts with one molecule of the reagent to form the complex. The following formula therefore is proposed for the boron complex *in solution*.



Beer's law and sensitivity. The boron complex obeys Beer's law over the concentration range of 1 to 5 γ of boron per 10 ml of solution, with a practical range of 1.2 to 4.2 γ , where the absorbances occur between 0.2 to 0.7 unit.

Using SANDELL'S⁶ expression for the sensitivity of a colorimetric reaction and the absorbance of 0.05 p.p.m. of boron (0.097), the sensitivity is found to be 0.0005 γ per square centimeter. However, the practical sensitivity, determined by measuring the absorbance of decreasing amounts of boron, was found to be 0.003 γ per square centimeter, *i.e.*, 1 part of boron in 300 million parts of solution when absorbance measurement is made in a 1-cm cell.

Effect of diverse ions. To determine the interferences by diverse ions, individual solutions were prepared containing 0.3 p.p.m. of boron, the reagent, and 500 p.p.m. of each ion to be tested. An increase or decrease of 0.010 in absorbance (1.8%) was chosen arbitrarily to represent an interference. If interference was noted, then more tests were made using lower concentrations of the diverse ion, until a change of less than \pm 0.010 absorbance unit was obtained.

This study shows that boron, especially when present in trace amounts, must be separated from many of the common metal ions, as well as oxidizing anions, before it can be determined accurately by this method. Table I lists the tolerances of the diverse ions investigated and the compounds employed in their preparation.

TABLE I
TOLERANCE TO DIVERSE IONS

Ion	Added as	Limiting concentration p.p.m.
Al ⁺ ³	Al ₂ O ₃	500
AsO ₄ ⁻³	Na ₃ AsO ₄	500
Ba ⁺ ²	BaCl ₂	500
Ca ⁺ ²	CaCl ₂	500
ClO ₄ ⁻	KClO ₄	0
Cl ⁻	KCl	500
Cr ⁺ ³	Cr ₂ (SO ₄) ₃	0
Co ⁺ ²	CoCl ₂	500
Cu ⁺ ²	CuSO ₄	500
C ₂ O ₄ ⁻²	Na ₂ C ₂ O ₄	<10
Fe ⁺ ³	Fe ₂ (SO ₄) ₃	0
F ⁻	CaF ₂	0
Ge ⁺ ⁴	GeO ₂	<3
IO ₄ ⁻	KIO ₄	0
K ⁺	KCl	500
Mn ⁺ ²	MnSO ₄	500
Na ⁺	NaCl	500
Ni ⁺ ²	NiSO ₄	0
NO ₃ ⁻	KNO ₃	0
NO ₂ ⁻	NaNO ₂	0
PO ₄ ⁻³	Ca ₃ (PO ₄) ₂	0
Sb ₂ O ₇ ⁻⁴	K ₂ H ₂ Sb ₂ O ₇	500
Sr ⁺ ²	SrCO ₃	500
Zn ⁺ ²	ZnCl ₂	500

Method II

Fig. 5 shows the absorbance curves of Compound II and of the boron complex

of compound II. All measurements were made against 96% sulfuric acid as a blank.

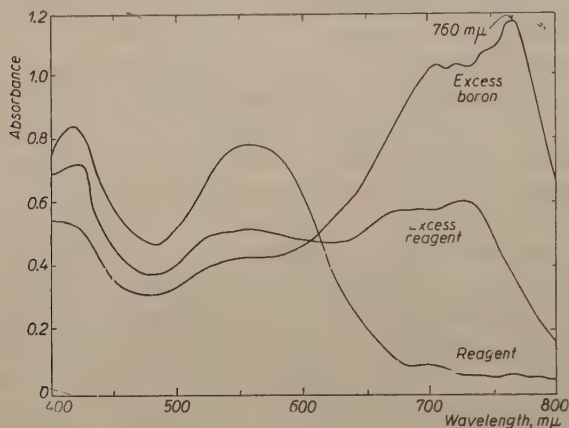


Fig. 5. Absorbance curves of Compound II and of its colored boron complex.

The colored complex has a maximum at 720 $m\mu$ when excess reagent is present and one at 760 $m\mu$ when excess boron is present. This shift in the maximum, when one or the other substance is varied in excess, is attributed to the formation of more than one complex.

In order to evaluate the use of the boron complex maximum (at 720 $m\mu$) as a means of determining small amounts of boron, a study was made of some of its important properties.

Effect of sulfuric acid concentration. The effect of the sulfuric acid concentration was determined by measuring the absorbances of solutions containing 4.0 γ of boron, 1.0 ml of reagent, heating for three hours at 130° C in an oven, and diluting to 10 ml volume with varying percentages of sulfuric acid. The results of this study proved to be the same as those for Compound I, *i.e.*, the sulfuric acid strength must be at least 96%.

Rate of reaction and stability of complex. The study on the rate of the reaction was carried out in the same manner as for Compound I. Results showed that the solutions must be heated for three hours at 130° C. Upon standing for 17 days, the complex showed only a 3.3% increase in absorbance, a color stability quite adequate for analytical use.

The boron complex in solution. The three methods mentioned above¹⁻⁵ were used in an attempt to establish the empirical formula of the complex *in solution*. All results were unsatisfactory. They indicate, however, that more than one complex exists and hence the two maxima obtained in Fig. 5.

Beer's law and sensitivity. The boron complex obeys Beer's law over the concentration range of 1 to 4 γ of boron per 10 ml of solution, with a practical range of 0.95 to 3.8 γ , where the absorbances occur between 0.2 to 0.7 unit.

Using SANDELL's⁶ expression for the sensitivity of a colorimetric reaction and the absorbance of 0.05 p.p.m. of boron (0.105), the sensitivity is found to be 0.0004 γ per square centimeter. However, the practical sensitivity, determined by measuring the absorbance of decreasing amounts of boron, was found to be 0.005 γ per square centimeter, *i.e.*, 1 part of boron in 200 million parts of solution when absorbance measurement is made in a 1-cm cell.

Effect of diverse ions. This study was carried out in the same manner as described above for Compound I. Tolerances to diverse ions were the same as those shown in Table I.

SEPARATION OF BORON

GOOCH⁷ found that alkali and alkaline-earth borates, on being distilled with absolute (acetone-free) methyl alcohol, give up their boron in the form of methyl borate, a liquid which boils at 65°C. If the methyl borate is brought into contact with a weighed amount of base in the presence of water, it is completely hydrolyzed. If, however, a small excess of base is not present, the ester will be converted to the unstable sodium metaborate⁸ instead of the stable sodium borate and boron will be lost when the distillate is evaporated.

The fact that comparatively small amounts of boric acid can be volatilized quantitatively from a methanol solution is probably due to the formation of complex compounds with the solvent molecules, the complexes being as volatile as the solvent itself. There is little question of forming an ester with HO-radicals and boric acid. This reaction involves the liberation of one molecule of water and the formation of a complex, the processes being very rapid and having properties of ester formation.

Esters of boric acid differ from most esters because they combine with one mole of an alcohol to give a monobasic acid⁹. This occurs because the boron atom lacks a pair of electrons. Thus, it can form a complex with a molecule of the alcohol by taking an unshared pair of electrons from the oxygen atom into its valence shell. This electron pair is held so strongly that the proton can be readily removed.

Standard leaf sample. In order to determine the conditions for the decomposition of the sample and the subsequent separation of the boron, it was necessary to have a large supply of a green leafy substance the boron content of which was accurately known. This was accomplished by procuring a large amount of spinach (2.72 kilograms), which is as representative of a boron-containing substance as any other green leafy vegetable. This spinach was dried under heat lamps until the moisture was removed. The crisp, dried leaves were crushed and ground in a large porcelain mortar with pestle. The crushed leaves were then mixed, so as to yield a homogeneous mixture, and stored in a large desiccator over P_2O_5 . The boron content was then accurately

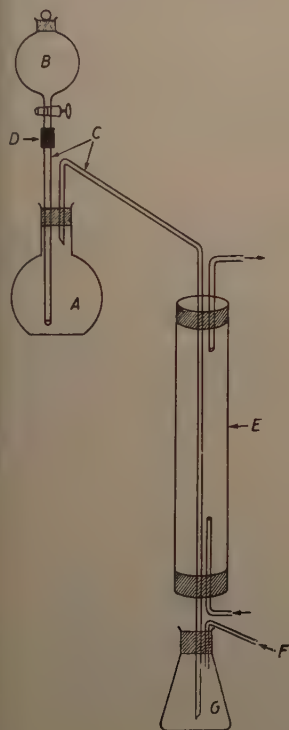


Fig. 6. Distillation apparatus.

- A 200 ml boron free flask
- B dropping funnel
- C 8 mm boron free glass tubing
- D polyethylene seal
- E condenser (borosilicate glass)
- F capillary tube exit
- G 250 ml boron free flask

determined. For this the titration of boric acid, in the presence of mannitol, was chosen. The ashing technique used was that prescribed by the A.O.A.C.¹⁰. The titrations were carried out with a Fisher Titrimeter equipped with a calomel-glass electrode system. The details of the titrations accord with those of HILLEBRAND AND LUNDELL⁸.

The sodium hydroxide solution used in the determination of the boron content of the standard leaf sample was standardized against samples of pure orthoboric acid.

Five samples of the dried spinach were titrated and gave values of 77.0, 74.0, 73.4, 71.1 and 70.0 p.p.m. of boron, respectively; an average value of 73.1 p.p.m.

PROCEDURE

Approximately 0.1 g samples are used for each analysis, depending on the boron content. The procedure is as follows: into a distilling flask (Fig. 6), the following substances are added — leaf sample, 1 g of calcium hydroxide, and 2 ml of 96% sulfuric acid. The flask is then connected to the distillation system. The receiving flask, containing 1 ml of 0.01*N* sodium hydroxide and 25 ml of distilled water, is then connected to the system. Two milliliters of 30% hydrogen peroxide are cautiously added to the distilling flask through the dropping funnel. When all organic matter has been destroyed, a paraffin bath is placed in contact with the flask. Then 100 ml of absolute methanol is added. The temperature of the bath is slowly raised to approximately 90° C, giving a slow but steady volatilization of the ester and excess methanol. The distillation is continued until no more liquid comes over. Remove the receiving flask, add 5 ml of *N* NH₄OH, shake well and evaporate the solution to dryness on a hot-plate (set on low temperature) with an infrared lamp suspended about 4 inches above the mouth of the flask. Cool the residue to room temperature, add the reagent solution, mix and measure the absorbance.

STANDARD DEVIATION

In order to determine the precision and standard deviation of the separation of boron by the new technique, a set of experimental values were interpreted statistically.

The results of twelve distillations were used for the interpretation. The sum of the squares of the 12 results, in per cent recovery, was totaled and also the square of the sum of the 12 results divided by *n*. The square root of the difference of these results divided by *n*-1 gives the standard deviation. Table II summarizes the data.

TABLE II
STANDARD DEVIATION DATA

Distillation No.	Boron present μg	Boron found μg	Recovery %
1	5.80	5.78	99.6
2	5.20	5.20	100.0
3	4.90	4.86	99.2
4	4.75	4.65	97.9
5	4.50	4.40	97.8
6	5.09	5.00	98.2
7	5.46	5.40	98.9
8	5.66	5.63	99.5
9	6.37	6.34	99.5
10	5.46	5.42	99.3
11	5.36	5.30	98.9
12	5.15	5.05	98.1
Standard deviation: 0.58%			Av. 98.9

APPLICATION OF PROCEDURE

Table III summarizes the results of five referee samples; four fruit tree leaves and one sample of alfalfa. The samples were obtained from the School of Agriculture, Michigan State College, East Lansing, Michigan. Our laboratory is one of about twenty cooperating in this referee program. These laboratories are located throughout the U.S.A.

TABLE III
RESULT OF ANALYSES OF STANDARD REFEREE SAMPLES

Sample type	Referee values	Boron found	Average
	p.p.m.	p.p.m.	p.p.m.
Apple —1	20.0—34.5	26.0	27.4
—2		28.8	
—3		25.8	
—4		26.7	
—5	av. 27.0	29.8	
Cherry—1	29.5—45.8	35.2	37.4
—2		38.0	
—3		36.4	
—4		39.0	
—5	av. 37.0	38.6	
Citrus —1	28.0—85.0	60.0	62.0
—2		54.2	
—3		69.3	
—4		62.0	
—5		59.5	
—6	av. 64.0	67.3	
Peach —1	17.0—50.0	42.0	38.4
—2		36.0	
—3		40.0	
—4		33.4	
—5		35.0	
—6	av. 36.0	44.0	
Alfalfa—1	26.8—35.0	32.0	32.1
—2		31.6	
—3	av. 32.0	32.8	

SUMMARY

Two new color reactions with boron are reported. Sensitive methods have been developed for their use. A new method for the decomposition of fruit tree leaves and alfalfa, and the subsequent separation of the boron is described.

The reagents are 5-benzamido-6'-chloro-1,1'-bis (anthraquinonyl) amine(I) and 5-*p*-toluidino-1,1'-bis (anthraquinonyl) amine(II). Concentrated (96%) sulfuric acid is used as the solvent. The formation of the boron complex of the reagents was found to be dependent on the following variables: time of heating, temperature, sulfuric acid content and the presence of diverse ions.

Solutions of the two complexes follow Beer's law over the boron range indicated: Compound I, 0 to 0.5 γ at wavelength of 635 $m\mu$ and Compound II, 0 to 0.4 γ at wavelength 720 $m\mu$. The sensitivities are 1 : 300,000,000 and 1 : 200,000,000, respectively. The standard deviation was calculated for the determination of boron with each compound. Results showed 0.002 absorbance unit, *i.e.*, 0.001 γ of boron for Compound I and 0.005 absorbance unit, *i.e.*, 0.002 γ of boron for Compound II.

The method of decomposing the leaves and alfalfa samples is based upon destroying all the organic matter with a mixture of 96% sulfuric acid and 30% hydrogen peroxide within the distilling flask. Boron is then distilled off as the volatile trimethyl ester. The standard deviation of the method is 0.58%.

RÉSUMÉ

Deux nouvelles réactions colorées du bore sont décrites. Des méthodes sensibles ont été mises au point pour leur emploi. Une nouvelle méthode est donnée pour la minéralisation des feuilles d'arbres fruitiers et de luzerne et pour la séparation du bore.

Ces réactifs sont: la 5-benzamido-6-chloro-1,1'-bis (anthraquinone) amine (I) et la 5-*p*-toluidino-1,1'-bis (anthraquinone) amine (II). L'acide sulfurique concentré (96%) est utilisé comme solvant. La formation des complexes de ces réactifs avec le bore dépend des facteurs suivants: durée du chauffage, température, teneur en acide sulfurique et présence de divers ions.

Les solutions de ces deux complexes suivent la loi de Beer pour les quantités de bore suivantes: composé I, 0 à 0.5 γ à la longueur d'onde de 635 $m\mu$ et composé II, 0 à 0.4 γ à 720 $m\mu$. Les sensibilités sont respectivement: 1 : 300,000,000 et 1 : 200,000,000. L'erreur a été calculée pour le dosage du bore avec chacun de ces composés. Les résultats ont donné 0.002 unité d'absorption, c'est-à-dire 0.001 γ de bore pour le composé I et 0.005 unité d'absorption, c'est-à-dire 0.002 γ de bore pour le composé II.

La méthode de minéralisation des feuilles et de la luzerne est basée sur la destruction de la matière organique par un mélange d'acide sulfurique à 96% et de peroxyde d'hydrogène à 30% dans un ballon à distiller. Le bore est ensuite distillé sous forme de son triméthylester volatil. L'erreur est de 0.58%.

ZUSAMMENFASSUNG

Es werden zwei neue Farbreaktionen für Bor beschrieben. Es wurden empfindliche Methoden für ihre Anwendung ausgearbeitet. Eine neue Methode für die Mineralisation von Obstbaumblättern und von Luzernen und für die Abtrennung von Bor wird gegeben.

Diese Reagenzien sind: das 5-Benzamido-1,1'-bis(anthrachinon) amine (I) und das 5-*p*-Toluidino-1,1'-bis (anthrachinon) amin (II). Konzentrierte Schwefelsäure (96%) wird als Lösungsmittel verwendet. Die Bildung der Komplexe dieser Reagenzien mit dem Bor, hängt von folgenden Faktoren ab: Dauer des Heizens, Temperatur, Gehalt an Schwefelsäure und Gegenwart von verschiedenen Ionen.

Die Lösungen dieser beiden Komplexe folgen dem Beerschen Gesetz für folgende Bormengen: Verbindung I, 0 bis 0.5 γ bei der Wellenlänge 635 $m\mu$ und Verbindung II, 0 bis 0.4 γ bei 720 $m\mu$. Die Empfindlichkeiten sind respektive: 1 : 300,000,000 und 1 : 200,000,000. Der Fehler wurde für die Bestimmung von Bor mit beiden Verbindungen berechnet. Die Resultate ergaben 0.002 Absorptionseinheit, d.h. 0.001 γ Bor für die Verbindung I und 0.005 Absorptionseinheit, d.h. 0.002 γ Bor für Verbindung II.

Die Methode der Mineralisation der Blätter und der Luzernen basiert auf der Zerstörung der organischen Substanzen mittels einer Mischung von Schwefelsäure zu 96% und Wasserstoffperoxyd zu 30% in einem Destillationskolben. Das Bor wird darauf in Form seines flüchtigen Trimethylesters destilliert. Der Fehler ist 0.58%.

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UNE MÉTHODE DE DOSAGE COLORIMÉTRIQUE DU PHOSPHORE DANS LES MATIÈRES ORGANIQUES

par

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INTRODUCTION

Pour doser une très petite quantité de phosphore, soit dans les matières organiques, soit dans les eaux naturelles, il faut d'abord minéraliser les échantillons et ensuite contrôler l'acidité et la concentration des sels de la solution à analyser. Cet exposé a pour but ^{principal} 1° de présenter un nouveau flacon de destruction des matières organiques permettant de minéraliser les échantillons sans aucun soubresaut; 2° de proposer l'emploi de l'oxyde hydraté de fer(III) pour la séparation du phosphate des autres sels présents. LEVINE *et al.*¹ indiquent l'utilisation possible de l'oxyde hydraté d'aluminium pour le dosage colorimétrique des phosphates dans l'eau.

PARTIE EXPÉRIMENTALE

Flacon de destruction des matières organiques

Pour éviter des pertes dues aux soubresauts lors de la minéralisation des matières organiques au moyen du flacon de Kjeldahl, K. IWASAKI² proposa un nouveau récipient.

Nous proposons ici l'utilisation d'un flacon (Fig. 1) où A est un tube en verre, B le flacon et C le réfrigérant présenté par SCHIRM³. A l'extrémité inférieure de A est fixé un tube ouvert, qui agit comme de la pierre ponce.

Mode opératoire

On introduit l'échantillon dans le flacon, on ajoute successivement 2 ml d'acide sulfurique (densité: 1.84), 5 mg de fer(III) (solution de chlorure de fer(III)) et 0.2 ml d'acide perchlorique. On chauffe le flacon en prenant garde à ne pas volatiliser l'acide sulfurique; on utilise un réfrigérant de SCHIRM³. La minéralisation est complète après deux heures, la présence du sel de fer(III) favorise considérablement la destruction.

On verse la liqueur après minéralisation complète dans un bécher de 100 ml et on ajoute 70 ml d'eau environ. On chauffe la solution à 70-80° C et on la neutralise par l'ammoniaque 4N, en employant le pourpre de bromocrésol comme indicateur. On agite. Après refroidissement, on

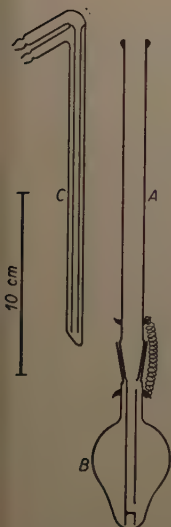


Fig. 1. Flacon à destruction des matières organiques.

filtre le précipité à l'aide d'un filtre de verre. On dissout le précipité dans 15 ml d'acide sulfurique *N*. On ajoute 1 ml de solution de molybdate d'ammonium à 2% et 1 ml de sulfate d'hydrazine à 0.5%; on complète la solution à 25 ml avec de l'eau distillée. On chauffe au bain-marie pendant 30 minutes (formation de bleu de molybdène) et on refroidit. On mesure la densité optique à 840 $m\mu$ ou 700 $m\mu$ à l'aide d'un spectrophotomètre.

Courbe d'étalonnage

Nous donnons la courbe d'étalonnage obtenue (Fig. 2).

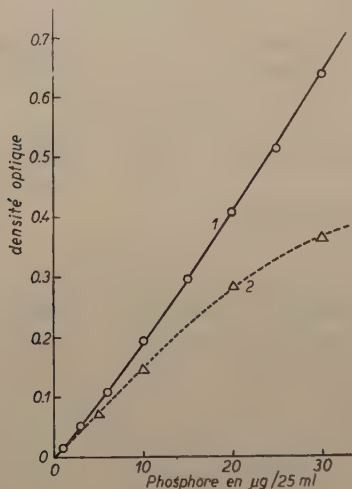


Fig. 2. Courbe d'étalonnage. Cuvette: 16 mm; longueur d'onde: 700 $m\mu$.
Courbe 1: cette méthode.
Courbe 2: sans emploi de la précipitation de $Fe(OH)_3$.

On donne également la courbe obtenue sans utiliser d'oxyde hydraté, comme collecteur de phosphate (on neutralise la solution minéralisée et on opère comme précédemment).

Exemples d'analyse

Comme on le voit dans le Tableau I, la méthode est quantitative.

TABLEAU I
EXEMPLES D'ANALYSE

Échantillon	Quantité prise	P ajouté en μg	P retrouvé en μg	P calculé en μg
Aiguille du pin (matière séchée)	10 mg	—	8.4	—
<i>id.</i>	10 mg	10	18.1	18.4
Oeuf de <i>Rana japonica</i>	1	—	18.8	—
<i>id.</i>	1	10	28.5	28.8
Eau d'un puits dans la Faculté des Sciences de Nagoya	125 ml	—	23.0	—
<i>id.</i>	125 ml	2.5	25.7	25.5
Eau du Courant Noir (Superficie)	200 ml	—	2.2	—
(34°51'N, 139°59'E)	200 ml	5	7.3	7.2
<i>id.</i>	200 ml	5	7.3	7.2

On peut l'appliquer aux échantillons d'eaux naturelles, dont quelques exemples sont donnés dans le même tableau.

Nous tenons à mentionner le nom du Professeur K. SUGAWARA, à qui va notre profonde gratitude pour son intérêt particulier et son encouragement incessant au cours de ces recherches.

RÉSUMÉ

1° On propose l'emploi de l'oxyde hydraté de fer(III) pour la séparation du phosphate dans une solution contenant d'autres sels.

2° On présente un nouveau flacon de destruction des matières organiques permettant de minéraliser les échantillons sans aucun soubresaut.

3° En employant l'oxyde hydraté de fer(III) et le nouveau flacon, on peut effectuer avec succès le dosage du phosphore, soit dans les matières organiques, soit dans les eaux naturelles.

SUMMARY

1° The use of hydrated ferric oxide is suggested for separating phosphate from a solution containing other salts.

2° A new flask is proposed, which can be used in the decomposition of organic matters. By means of this flask, we can carry out the mineralization without any bumping.

3° By using hydrated ferric oxide and the new flask, we can successfully carry out the determination of phosphorus in natural waters as well as in organic matter.

ZUSAMMENFASSUNG

1° Die Verwendung des Ferrihydroxyds für die Abtrennung des Phosphates aus einer, auch andere Salze enthaltenden Lösung wurde vorgeschlagen.

2° Eine neue Flasche wurde beschrieben, die für die Zersetzung der organischen Substanzen gebraucht wird. Mittels dieser Flasche kann die Mineralisierung ohne Stossen ausgeführt werden.

3° Durch Anwendung des Ferrihydroxyds und der neuen Flasche, kann der Phosphor in organischen Substanzen und in natürlichem Wasser erfolgreich bestimmt werden.

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COLORIMETRIC DETERMINATION OF GLUTAMIC ACID IN PROTEIN HYDROLYSATES

by

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A colorimetric method for the determination of glutamic acid in protein hydrolysates was described in a previous communication¹. The method was based on a colour reaction given by pyrrolidonecarboxylic acid on heating with hydroxylamine and subsequent treatment with ferric chloride. Since glutamic acid is almost completely converted into pyrrolidonecarboxylic acid at 125° and pH 3-4, this colour reaction can be used for the quantitative determination of glutamic acid in protein hydrolysates.

The method presented here is based on the findings of SACHS AND BRAND² that the lactone formed on treating glutamic acid with nitrous acid can be estimated colorimetrically by the procedure described by HESTRIN³. We found that as little as 2/3 of a micromole of glutamic acid could be determined accurately by this method using a Klett-Summerson photoelectric colorimeter.

Glutamic acid contained in protein hydrolysates was adsorbed (together with aspartic acid) on Amberlite IR-4B columns at pH 3-4 and subsequently eluted with *N* hydrochloric acid as described by MORRIS AND STUCKEY⁴. The eluates were treated with nitrite and the lactone formed from glutamic acid estimated colorimetrically by HESTRIN's procedure. The values obtained with various proteins were in good agreement with those obtained by the colorimetric method previously described¹.

EXPERIMENTAL

2 g of protein were hydrolysed by refluxing with 20 ml of hydrochloric acid (1:1) in a stirred oil bath at 120-125° for 35 hours. 1 g of purified charcoal was added and heating continued for 1 hour. After cooling, water was added, the hydrolysate filtered and the residue washed with water. The filtrate was concentrated *in vacuo*, some water added and the solution was again evaporated *in vacuo*, this procedure being repeated 1 or 2 times. The dry residue was dissolved in water to a volume of 50 ml. 5 ml aliquots were adjusted to pH 3.5-4 by addition of 3.5*N* NaOH and water was added to a volume of 15 ml. 5 ml of this solution was transferred to the top of an Amberlite IR-4B column, prepared in the manner described by MORRIS AND STUCKEY⁴. The resin (mesh size 40-60) was treated with dilute hydrochloric acid and washed with water by decantation until the pH of the washing was 3-4. The resin was then transferred to a glass tube of about 1 cm internal diameter to a height of 15 cm and again washed with water until the pH of the effluent was between 3 and 4. The hydrolysate sample was allowed to run through the column at a rate of 1-2 ml per minute. The effluent was again passed through the column, which was then washed

with water (about 40 ml) until a portion of the washings no longer gave a colour reaction with ninhydrin. The adsorbed aminodicarboxylic acids were eluted with 100 ml of *N* HCl. The eluate was concentrated to dryness *in vacuo* and the residue dissolved in water (total volume 25 ml). In accordance with the procedure employed by SACHS AND BRAND², a 5 ml portion of this solution was transferred to a 25 ml volumetric flask, 1 ml of glacial acetic acid and 2 ml of sodium nitrite solution (800 g sodium nitrite per liter of water) were added and the mixture maintained at 25° for 10 minutes. 10 ml of 2*M* hydroxylamine hydrochloride was added dropwise whilst cooling the flask with ice water. The flask was filled up to the mark with water. 3 ml aliquots of this solution were added to a solution containing 1 ml of 2*M* hydroxylamine hydrochloride and 2 ml of 3.5*N* NaOH. After 4 minutes, 1.65 ml HCl (1:2) was added (the pH being now 1-1.2) and the mixture brought to a final volume of 10 ml by addition of a 0.37*M* solution of ferric chloride in 0.1*N* HCl. The colour produced was immediately measured in a Klett-Summerson photoelectric colorimeter with filter No. 54. For comparison, standard glutamic acid (or glutamic acid hydrochloride) solutions were treated in the same manner as the solutions of the concentrated eluates. The results obtained with various amounts of glutamic acid are given in Fig. 1. A complete recovery of glutamic acid was obtained when its standard solutions were passed through Amberlite IR-4B columns subsequently eluted with *N* HCl.

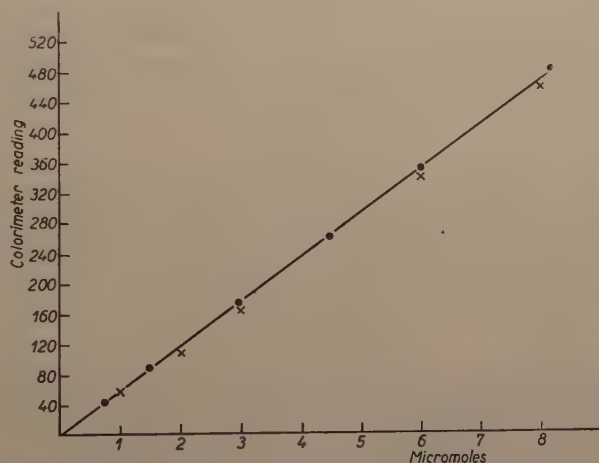


Fig. 1. Optical density (Klett-Summerson colorimeter reading) of hydroxamic acid-iron complex obtained from a) glutamic acid treated with nitrous acid (•); b) succinic anhydride (x).

The figures given in TABLE I are average values obtained from 3 separate hydrolysates of each protein. The results were calculated for the dry protein. Moisture was estimated by drying the proteins *in vacuo* over phosphorus pentoxide at 100°.

TABLE I

GLUTAMIC ACID CONTENT OF PROTEINS (PER CENT)

Protein	Found	Previous findings ¹
Casein*	22.1	23.1
Edestin**	20.5	20.0
Zein**	26.3	25.3
Fibrin**	15.7	16.5

* Fat free, The British Drug Houses Ltd., London.

** Nutritional Biochemicals Corporation, Cleveland, Ohio.

It may be of interest to note that the values obtained for glutamic acid by the colorimetric method correspond closely to those given by succinohydroxamic acid as indicated in Fig. 1. The values for succinohydroxamic acid were obtained as follows. A stock solution of succinohydroxamic acid was prepared by the procedure of LIPMANN AND TUTTLE⁵. Hydrochloric acid and water were added to aliquots containing various amounts of succinohydroxamic acid to produce a pH of 1-1.2 and a final volume of 7.65 ml. Ferric chloride was added to a final volume of 10 ml and the colour produced measured as in the glutamic acid determination. It may be recalled that glutamohydroxamic acid was found to give colorimetric values with ferric chloride which were quite close to those obtained with succinohydroxamic acid⁶.

SUMMARY

Glutamic acid contained in protein hydrolysates was adsorbed on Amberlite IR-4B columns at pH 3-4 and eluted with *N* HCl. Addition of nitrite to the eluates converted glutamic acid into the corresponding lactone of hydroxyglutaric acid. Hydroxylamine reacted with this lactone to give a hydroxamic acid, which was determined colorimetrically following the addition of ferric chloride.

RÉSUMÉ

L'acide glutamique, contenu dans les protéines hydrolysées, est adsorbé sur des colonnes d'Amberlite IR-4B à un pH 3-4 et ensuite élué avec l'acide chlorhydrique normal. L'addition de nitrite convertit l'acide glutamique en lactone correspondante de l'acide hydroxyglutarique. L'hydroxylamine réagit avec cette lactone en donnant un acide hydroxamique que l'on dose colorimétriquement après addition de chlorure de fer(III).

ZUSAMMENFASSUNG

Die in Proteinhydrolysaten enthaltene Glutaminsäure wird auf Amberlite-IR-4B-Kolonnen bei pH 3-4 adsorbiert und mit normaler Salzsäure eluiert. Zugabe von Nitrit zu den Eluaten verwandelt die Glutaminsäure in das entsprechende Oxyglutarsäurelaktone. Letzteres wird durch Hydroxylamin in eine Hydroxamsäure verwandelt, die nach Zugabe von Eisen(III)-chlorid kolorimetrisch bestimmt wird.

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HIGH-FREQUENCY INSTRUMENTATION*

by

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INTRODUCTION

High-frequency titrations are carried out in a dielectric vessel having external metal electrodes connected to a high-frequency oscillator. The metal electrodes are separated from the solution in the titration cell by the walls of the titration vessel, usually glass. Changes in the conductivity or in the dielectric constant (specific inductive capacity) of the solution in the cell cause changes in the oscillator circuit which can be measured and plotted against the volume of titrant added. The principles of high-frequency titrimetry have recently been reviewed by a number of authors^{1,2,6,8,9,11,12}. Several studies of high-frequency titration cell parameters have been made^{3,8,9}.

A disadvantage of high-frequency titrimeters is that the sensitivity to concentration changes depends on the geometry of the cell containing the sample being titrated, as well as the frequency of the instrument. In the present work the effect of cell geometry on the region of sensitivity was investigated.

Apparatus

The high-frequency instruments used were the commercially available Sargent Chemical Oscillometer Model V¹¹ and a laboratory-built apparatus based on a crystal oscillator circuit⁴. The Oscillometer responds primarily to changes in the effective capacitance in the titration cell circuit. The other titrimer was designed to respond to either effective capacitance, or to effective conductance changes in the titration cell circuit. A change in electrolyte concentration causes a change in grid bias voltage which is measured with a voltmeter. A cell adapter consisting of variable capacitors and single-pole double-throw switches in a metal cabinet permitted various types of cells to be used with either instrument⁵.

High-frequency conductivity cell

A high-frequency cell may be considered in terms of its equivalent electrical circuit, shown in Fig. 1, A. R_s and C_s represent the resistance and capacitance which would exist in the cell circuit if the metal electrodes were in contact with the solution. C_c is composed of two capacitors in series, each having one of the metal

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electrodes for one plate, the wall of the glass vessel for a dielectric and the surface of the solution in contact with the glass for another plate.

R_s and C_s vary with the resistivity and dielectric constant, respectively, of the solution in the cell. C_c is constant for a given cell. For a titration cell with electrodes of the same size and shape, the value of C_c varies directly as the area of the metal electrodes and the dielectric constant of the material of which the container is constructed and inversely as the thickness of the wall of the container.

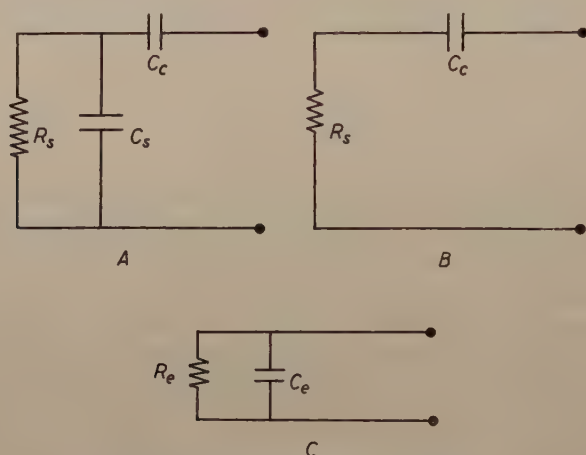


Fig. 1. Equivalent high-frequency cell circuits.
 A. Equivalent electrical circuit of a high-frequency cell.
 B. Simplified series equivalent circuit.
 C. Simplified parallel equivalent circuit.

A cell was constructed having physical dimensions such that C_s was made insignificant. For this cell the simplified series equivalent circuit, Fig. 1, B, applies. This was accomplished by using a long, narrow glass tube as the solution container with two thin metal bands as outer electrodes. The capacitor C_s then consisted effectively of two thin discs separated by a dielectric. From the equation for parallel plate capacitors,

$$C_s = \frac{K_s A}{4 \pi d} \quad (1)$$

it is seen that, although the dielectric constant (K_s) of the interspace is that of the solution, the area (A) of the plates is quite small and the distance between the plates (d) is large, so that C_s is made to approach zero. This arrangement would have a relatively large edge effect but the fringing would have no influence on the value of C_s since this part of the field passes through air. The overall effect, therefore, is equivalent to three capacitances in parallel. Two of these represent capacitors having air and glass as dielectrics and are constant for a given cell. Only C_s changes with the dielectric constant of the solution, and the value of C_s is made to approach zero.

Since C_c is constant for a given titration cell and effectively the only variable in the simplified series equivalent circuit is R_s , this cell should respond almost wholly

to changes in the conductivity of the solution. Changes in the dielectric constant of the sample solution should have no appreciable effect on the equivalent circuit. Such a cell was tested with benzene, 1,4-dioxane, chloroform, acetone, methyl alcohol, distilled water, 0.001*N* and 0.1*N* potassium chloride, saturated sodium chloride, concentrated hydrochloric acid and mercury. The value of C_s with water (25°C) as dielectric was about 1% of the value of C_e . Recently a similar conductivity cell has been used for the radio-frequency measurement of the salinity of ocean water⁷.

Response curves

The response curve of a high-frequency titration apparatus is a plot of the property measured by the instrument *versus* the normality or electrolytic conductance of the solution contained in the titration cell. Response curves of instrument readings *versus* dielectric constant can be made. Instruments, like the Sargent Oscillometer, which measure changes in effective capacity in the titration cell circuit display an S-shaped response curve, whereas the instruments which measure conductance loss show a U-shaped curve.

The basis for these response curves can be seen by a consideration of the simplified series equivalent cell circuit shown in Fig. 1, B. In this circuit R_s is inversely proportional to the electrolytic conductance of the solution in the titration cell. C_e is constant for a given titration cell.

The impedance of the titration cell circuit may be measured at the terminals of the titration cell in terms of the parallel admittance components, conductance and capacitive susceptance. The equivalent circuit of Fig. 1, B is shown in Fig. 1, C in terms of the parallel admittance components. R_e and C_e are the effective parallel resistance and capacitance of the simplified series equivalent titration cell circuit.

Equations relating C_e and R_e to C_s and R_s in the simplified series equivalent circuit are given below¹⁰.

$$C_e = \frac{1}{4 \pi^2 f^2 C_s \left[R_s^2 + \frac{1}{4 \pi^2 f^2 C_s^2} \right]} \quad (2)$$

$$R_e = \frac{R_s^2 + \frac{1}{4 \pi^2 f^2 C_s^2}}{R_s} \quad (3)$$

The height of the S-shaped response curve of effective-capacity measuring instruments is determined by the value of C_e . High sensitivity of such instruments occurs in the vicinity of the inflection point of the S-shaped response curve and the most sensitive region usually covers only a ten-fold range of concentration.

At the inflection point, where the second differential, $\frac{d^2 C_e}{d R_s^2}$ of equation (2)

$$\text{equals zero, } R_s = \frac{\sqrt{3}}{6 \pi f C_e} \quad (4)$$

Thus for instruments responding to changes in effective capacitance in the titration cell circuit, high sensitivity occurs in the range where R_s is nearly equal to $\frac{\sqrt{3}}{6 \pi f C_e}$. At the inflection point $C_e = 3/4 C_s$.

If $\log R_s$ is plotted against C_e , the inflection point of the curve occurs at the mid-point, the point at which $C_e = \frac{1}{2} C_e$. At this point $R_s = \frac{1}{2 \pi f C_e}$. (5)

The C_e versus $\log R_s$ curve is symmetrical with respect to the point $R_s = \frac{1}{2 \pi f C_e}$, $C_e = \frac{1}{2} C_e$.

The conductance loss curve has a dip at the point at which the maximum electrical energy is dissipated as heat. The minimum in the response curve, which may be obtained by equating the first differential of equation (3), $\frac{dR_s}{dR_s}$, to zero, occurs

when $R_s = \frac{1}{2 \pi f C_e}$. At this point, the point of minimum parallel equivalent resistance, $R_e = 2 R_s$, and $C_e = \frac{1}{2} C_e$. (6)

Instruments measuring conductance loss changes are sensitive in the regions on either side of the minimum in the response curve. Each of these regions is wider than the sensitive region of the S-shaped response curve of instruments responsive to changes in effective capacity and thus concentration is less critical with instruments measuring conductance loss.

The relation of response curves to the physical dimensions of high-frequency cells

It can be shown that concentration limitation can be overcome by varying the physical dimensions of the high-frequency titration cells. For a cylindrical cell and sample solution with a fixed specific conductance or fixed specific volume resistivity, the equation $R_s = \rho_s l / \pi r^2$ (7) can be applied as an approximation. Since the specific resistance (ρ_s) and π are constant, R_s varies directly with the cell length (l) and inversely with the square of the inside radius (r^2). This formula does not take into account the fact that in the columns of the solution surrounded by the metal electrodes there are effectively an infinite number of infinitesimally small capacitors. Electrically, this is somewhat similar to the phenomenon of characteristic impedance encountered in transmission lines. However, the approximation is valid. Progressively varying the electrode separation distance, for a given cell tube and sample solution, or varying the inside diameter of the titration vessel, for a constant electrode length and electrode separation distance, shifts the useful concentration regions of the response curves.

The external electrode itself can be considered as the outer plate of a coaxial cylindrical capacitor and, neglecting fringe effects, equation (8) gives the capacitance of C_e for electrodes of equal length.

$$C_e = \frac{Kh}{4 \ln \frac{r+g}{r}} \quad (8)$$

K is the dielectric constant of the interspace, h is the length of the metal electrode, r is the inside radius of the titration tube and g is the thickness of the cell wall. The value of C_e varies directly with the length of the electrodes and inversely with

the thickness of the cell wall. Increasing the length of the metal electrodes or decreasing the cell wall thickness magnifies the change in electrical properties measured and thus gives a greater rise in the response curves.

Experimental results

Studies were made of the significance of the physical dimensions of high-frequency titration cells and the results confirmed the theoretical predictions. Cells of from 3 to 65 mm outside diameter glass tubing were used. Metal bands (copper, aluminium) of from 2.5 to 12.5 cm length served as external electrodes. The electrode separation distances ranged from 1.5 to 60 cm.

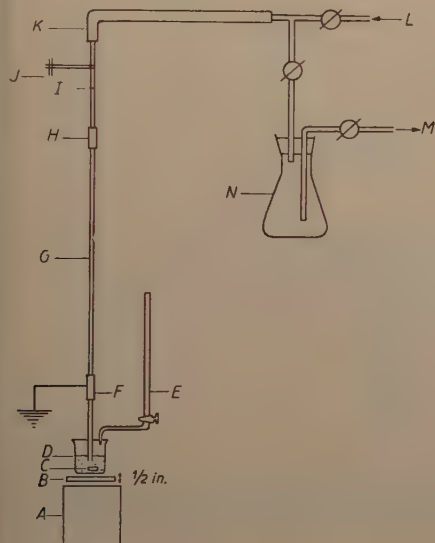


Fig. 2. High-frequency titration cell apparatus.

- A. Magnetic stirrer.
- B. Thermally and electrically insulating support.
- C. Stirring bar.
- D. 150-ml beaker.
- E. Burette.
- F. Grounded electrode.
- G. Glass titration tube.
- H. Sensitive electrode.
- I. Liquid level mark.
- J. Plastic clamp.
- K. Neoprene tubing.
- L. Air or nitrogen inlet.
- M. Aspirator outlet.
- N. Partially evacuated flask.

The experimental setup for the narrower cells is illustrated in Fig. 2. After each increment of titrating reagent was added to the sample, the solution was thoroughly stirred, a portion was drawn up into the glass tubing and its effective conductance or capacitance measured by

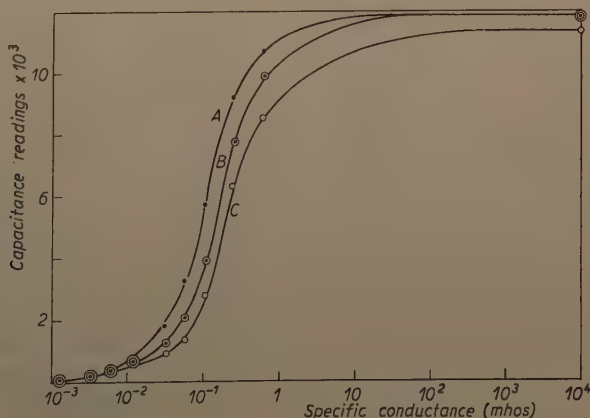


Fig. 3. Effect of electrode separation distance on high-frequency response curves.

9-mm flint glass tubing. 6.3-cm aluminium foil electrodes.

- A. 30-cm electrode separation distance.
- B. 46-cm electrode separation distance.
- C. 61-cm electrode separation distance.

the high-frequency method. The liquid was then returned to the bulk solution and the process repeated. The larger diameter titration cells were in the form of test tubes. Both air and magnetic stirring were employed.

The effect of varying the electrode separation distance for a glass tube of constant diameter is shown in Fig. 3. Increasing the distance between the electrodes shifts the inflection point of the curve to higher electrolyte concentrations.

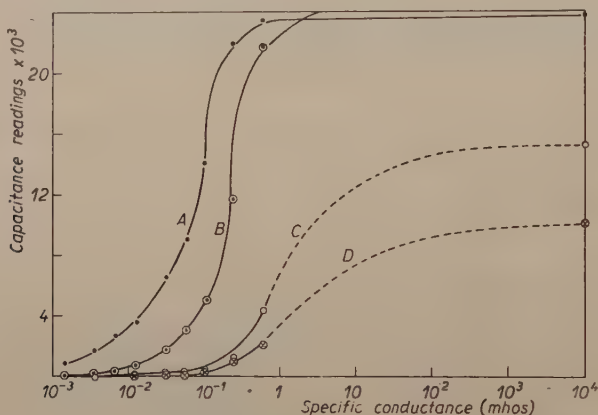


Fig. 4. Effect of cell diameter on high-frequency response curves (apparatus of Fig. 2). 30.5-cm electrode separation distance. 12.7-cm aluminium foil electrodes.

- A. 13-mm glass tubing.
- B. 9-mm glass tubing.
- C. 4-mm glass tubing.
- D. 3-mm glass tubing.

The effect of varying the diameter of the titration cell is shown in Figs. 4 and 5. Increasing the diameter of the cell shifts the inflection point of the curve to lower electrolyte concentrations.

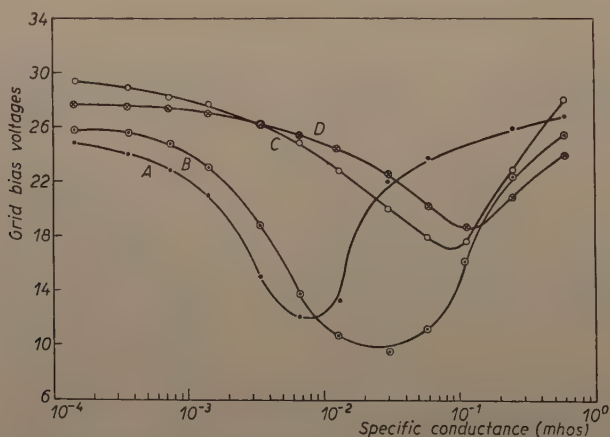


Fig. 5. Effect of cell diameter on high-frequency response curves (apparatus of Fig. 2). 3-cm aluminium foil electrodes. 30.5-cm electrode separation distance.

- A. 13-mm glass tubing.
- B. 9-mm glass tubing.
- C. 4-mm glass tubing.
- D. 3-mm glass tubing.

Table I summarizes the extremely wide concentration range that can be investigated when both the distance of separation of the electrodes and the diameter of the cell are varied. The sensitive regions of the response curves vary from specific conductances corresponding to $2 \cdot 10^{-3}N$

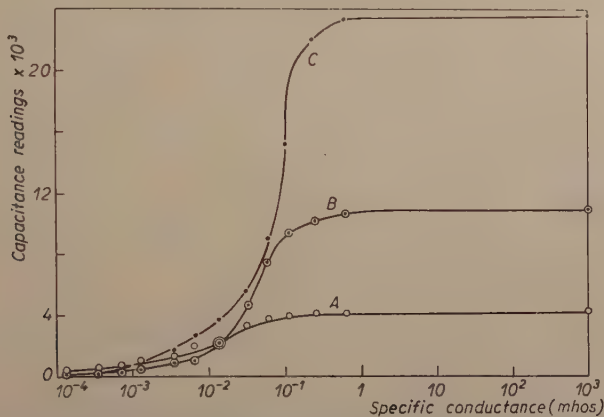


Fig. 6. Effect of electrode length on high-frequency response curves. 13-mm Pyrex glass tubing. 30.5-cm electrode separation distance.
A. 2.5-cm electrodes.
B. 6.3-cm electrodes.
C. 12.7-cm electrodes.

KCl solutions to concentrated hydrochloric acid. Figs. 6 and 7 verify the assumption that the value of C_c is related directly to the length of the electrodes and inversely to the cell wall thickness.

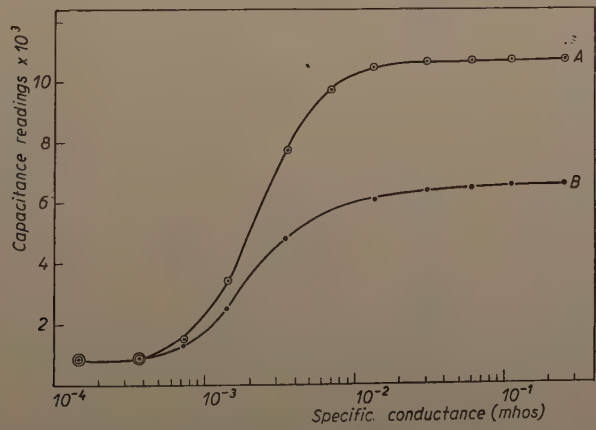


Fig. 7. Effect of wall thickness on high-frequency response curves. 29-mm O.D. Pyrex test tube cells. 3-cm aluminium foil electrodes. 10-cm electrode separation distance.
A. 2.5-mm wall thickness.
B. 3.9-mm wall thickness.

Fig. 8 shows a family of response curves obtained with the Sargent Oscillometer connected to different mica capacitors in series with various values of non-inductive resistors. Instrument

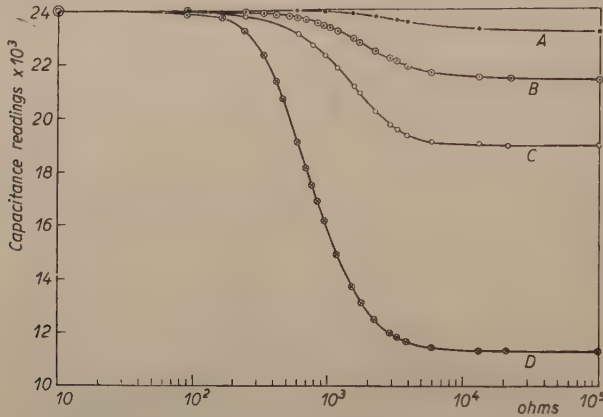


Fig. 8. Response curves for series resistance-capacitance circuits.

- A. $C_c = 5$ mmfd
- B. $C_c = 12$ mmfd
- C. $C_c = 24$ mmfd
- D. $C_c = 50$ mmfd

response, given in units on the Oscillometer, where each unit equals about 0.005 mmfd, is theoretically related to the capacitor and resistor values by equation (2). Theoretical response curves, calculated from equations (2) and (3) are given in Figs. 9 and 10.

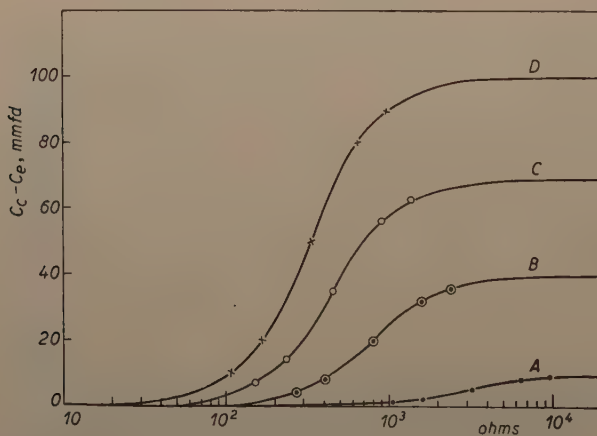


Fig. 9. Plot of equation 2, with $f = 5.10^6$ C.P.S.

- A. $C_c = 10$ mmfd
- B. $C_c = 40$ mmfd
- C. $C_c = 70$ mmfd
- D. $C_c = 100$ mmfd

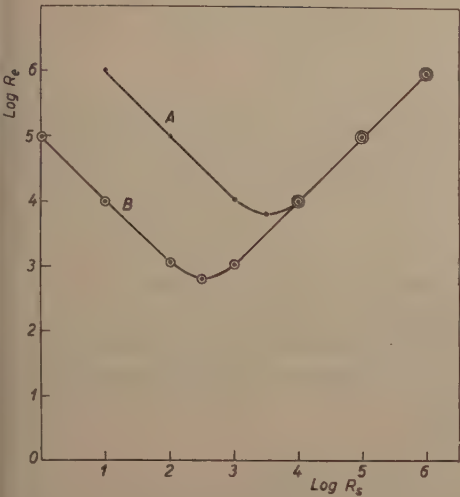


Fig. 10. Plot of equation 3, with $f = 5 \cdot 10^6$ C.P.S.
A. $C_c = 10$ mmfd
B. $C_c = 100$ mmfd

DISCUSSION

The families of curves in Figs. 4, 8, and 9, obtained by plotting response of the Oscillometer to a number of cylindrical high-frequency cells containing various conductive solutions, by plotting response of the Oscillometer to series resistance-capacitance circuits and by plotting the theoretical response curves show that, as an approximation for instruments

which measure effective capacitance changes, a cylindrical high-frequency cell can be described in terms of the simplified series equivalent circuit of Fig. 1, B.

The families of curves in Fig. 10, obtained by plotting equation (3) and in Fig. 5, obtained by plotting the response of the conductance-loss instrument to a number of cylindrical high-frequency cells containing conductive solutions show that the same considerations hold for this type of instrument.

TABLE I

EFFECT OF TITRATION CELL DIAMETER SARGENT OSCILLOMETER

Outside cell diameter, mm	Electrode separation distances, cm		Approximate effective concentration region
		Specific conductance (mho)	Example
3	30.5	$6 \cdot 10^{-1}$	Concentrated HCl
4	30.5	$6 \cdot 10^{-1}$	Concentrated HCl
9	30.5	$2.5 \cdot 10^{-1}$	Saturated NaCl
13	30.5	$1.1 \cdot 10^{-1}$	1.0 <i>N</i> KCl
25	10.0	$4.1 \cdot 10^{-3}$	0.03 <i>N</i> KCl
29	10.0	$2.8 \cdot 10^{-3}$	0.02 <i>N</i> KCl
38	10.0	$1.4 \cdot 10^{-3}$	0.01 <i>N</i> KCl
40	1.5	$7.2 \cdot 10^{-4}$	0.005 <i>N</i> KCl
50	1.5	$5.8 \cdot 10^{-4}$	0.004 <i>N</i> KCl
65	1.5	$2.9 \cdot 10^{-4}$	0.002 <i>N</i> KCl

For any conductance cell the ratio of distance between electrodes to their cross-sectional area is a fixed quantity and is called the cell constant (k). Therefore, as an approximation, cylindrical high-frequency cells having electrodes at the ends may be considered to have a cell constant which relates the specific conductance

of the solution in the cell to the value of R_s in the series equivalent cell circuit. The

$$\text{exact relationship is } R_s = \frac{k}{L_s} = \frac{l}{\pi L_s r^2}, \quad (9)$$

where R_s is the series equivalent resistance of the titration cell containing a solution of specific conductance L_s ($1/\rho_s$), k is the cell constant, l is the length of the liquid column between the electrodes of the high-frequency cell and r is the inside radius of the cylindrical cell.

Since the inflection point of the semi-logarithmic plot of ΔC_c versus R_s for instruments measuring effective capacitance changes occurs at the value of R_s given by equation (5), the physical dimensions of a cylindrical high frequency cell for which maximum sensitivity will be obtained with electrolytes of a given specific conductance can be determined. On substituting equations (8) and (9) in equation (5), it is

$$\text{found that } L_s = \frac{K f h l}{2r^2 \ln \frac{r+g}{r}}. \quad (10)$$

Thus, in order to design a high-frequency titration cell suitable for a given titration, the specific conductance of the solution at the end-point of the titration is determined or estimated. From this value the physical dimensions of the cell can be determined using equation (10).

Constant-temperature systems

Very accurate high-frequency measurements require some method of temperature regulation, although this is generally ignored. The conductivity of solutions is dependent on the temperature and increases rapidly with rise in temperature (2% to 2.5% per degree C for aqueous solutions). In addition the dielectric constants of liquids fall with increased temperature.

Due to its high dielectric constant water seems unsuitable as a constant temperature liquid for high-frequency measurements involving organic compounds. Moreover, contamination of aqueous systems with resulting change in conductance is difficult to avoid. However, constant-temperature systems were devised to permit both aqueous and non-aqueous liquids to be used as circulating media.

For the narrow tubing titration cell apparatus, Fig. 2, a glass beaker surrounded by a jacket through which constant-temperature liquid was pumped gave excellent temperature regulation. The beaker was lowered to remove the narrow glass tube from the bulk of the solution and the measurements were taken rapidly. Since the beaker is not electrically connected to the titrimeter cell during readings, water can be used as a constant temperature medium.

With the larger diameter test-tube titration cells satisfactory temperature regulation was obtained by making the lower electrode a hollow copper jacket or simply tightly wrapping copper tubing around the one metal foil electrode. Since this electrode was grounded, constant-temperature water could be used as the circulating liquid. For a difference of $\pm 3^\circ \text{C}$ between room temperature and bath temperature, these devices were capable of regulating the sample temperature within $\pm 0.1^\circ \text{C}$. Some temperature regulation was obtained by circulating constant-temperature water through the grounded inner electrode of a Sargent Type B titration cell.

SUMMARY

The present work was undertaken to overcome the disadvantage of the limited concentration range of high-frequency measurements. Instruments which respond to either effective capacitance or effective conductance changes were used. A cell was designed to minimize the dielectric constant contribution of the solution, and respond only to conductance. Studies on the significance of the physical dimensions of high-frequency titration cells were carried out. Progressively varying the electrode separation distance or the diameter of the titration vessel shifted the useful concentration regions of the response curves. Increasing the length of the metal electrodes or decreasing the cell wall thickness magnified the response of the effective concentration regions. An equation was derived relating the specific conductance of the sample solution to the physical dimensions of the high-frequency cell necessary for maximum sensitivity. Constant-temperature systems were devised to permit both aqueous and non-aqueous liquids to be used as circulating media.

RÉSUMÉ

Ce travail a été entrepris pour pallier à l'inconvénient des limites de concentrations des mesures de haute fréquence. Des instruments répondant aux changements de capacitance effective ou de conductance effective ont été utilisés. Une cuve est proposée pour diminuer au maximum l'effet de la constante diélectrique de la solution, et répondre seulement à la conductance. Des études sur le rôle des dimensions physiques des cuves de titration à haute fréquence ont été effectuées. En faisant varier progressivement la distance entre les électrodes ou le diamètre du récipient de titration, on peut changer les limites de concentrations utilisables des courbes. En augmentant la longueur des électrodes métalliques ou en diminuant l'épaisseur des parois de la cuve, on peut étendre les limites de concentrations effectives. Une équation a été établie donnant la relation entre la conductance spécifique de la solution à analyser et les dimensions de la cuve de haute fréquence nécessaire pour un maximum de sensibilité. Des systèmes à température constante, à circulation de liquides aqueux ou non aqueux, ont été proposés.

ZUSAMMENFASSUNG

Diese Arbeit wurde unternommen, um die Schwierigkeiten zu überwinden, welche von den Konzentrationsgrenzen der Hochfrequenzmessungen herrühren. Es wurden Instrumente verwendet, welche den Änderungen der effektiven Kapazität und der effektiven Konduktanz angepasst sind. Es wird eine Zelle vorgeschlagen, um den Effekt der dielektrischen Konstante der Lösung am meisten zu verringern und um nur die Konduktanz allein wirken zu lassen. Es wurden Untersuchungen ausgeführt über die Rolle der physikalischen Dimensionen der Hochfrequenztitrationszelle. Indem man progressiv die Distanz zwischen den Elektroden oder den Durchmesser des Titrationsgefäßes variiert, kann man die gebräuchlichen Konzentrationsgrenzen der Kurven ändern. Wenn man die Metallelektroden verlängert oder wenn man die Wanddicke der Zelle verringert, kann man die effektiven Konzentrationsgrenzen ausdehnen. Es wurde eine Gleichung aufgestellt, welche die Abhängigkeit gibt, zwischen der spezifischen Konduktanz der zu analysierenden Lösung und den Dimensionen der Hochfrequenzzelle, welche notwendig ist um ein Maximum an Empfindlichkeit zu erreichen. Systeme mit konstanter Temperatur, in denen wässrige oder nicht wässrige Flüssigkeiten zirkulieren können, wurden vorgeschlagen.

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HIGH FREQUENCY TITRATIONS INVOLVING CHELATION WITH
ETHYLENEDIAMINETETRAACETIC ACID

V. COMPLEXATION WITH RARE EARTHS

by

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It has already been established that the rare earth metals form stable complexes with ethylenediaminetetraacetic acid. BRINTZINGER, THIELE AND MILLER obtained the complexes $\text{LaH}(\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8)$ and $\text{NdH}(\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8)^1$, and VICKERY² prepared various lanthanon group complexes and studied their absorption spectra. The formation of ethylenediaminetetraacetic acid complexes has also been utilized in the separation of rare earths^{3,4,5,6}. The chemical and physical properties of ethylenediaminetetraacetic acid complexes of the rare earth metals have been studied by potentiometric and electrometric titrations, spectrophotometry, electrophoresis and other physico-chemical approaches^{6,7,8}.

The present investigation was undertaken to study complexation of rare earths by ethylenediaminetetraacetic acid through the use of high frequency methods and to establish the possibilities of high frequency titrations for the quantitative determinations of these metals.

EXPERIMENTAL

Chemicals. Lanthanum, cerium(III), neodymium, and praseodymium nitrates, and gadolinium bromate were used. With the exception of gadolinium bromate, these salts were of reagent grade with certified purities of 99.9%. The purity of the gadolinium was not indicated nor was the nature of impurities given. It was assumed that the principal contaminants were rare earths and, because of the nature of the studies, these would not introduce serious error. All of the rare earth solutions were standardized by precipitation of the respective rare earth oxalates with subsequent conversion and weighing as the corresponding oxides. Reagent grade ethylenediaminetetraacetic acid (Versene) and disodium ethylenediaminetetraacetate were used. Standard solutions of these reagents were checked against primary standard calcium and copper salts using high frequency titrations as described previously⁹. In the studies of the quantitative determination of the rare earths, further standardization of the disodium ethylenediaminetetraacetate was made by titration against known amounts of lanthanum.

Apparatus. A Sargent Model V Oscillometer was used for all high frequency measurements. Titrations were performed using the large cell (100 ml). Hydrogen ion concentrations were measured using a Beckman Model G pH meter.

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Determination of reacting ratios of rare earth metals to ethylenediaminetetraacetic acid

The ratio of reactants was followed by titration of the hydrogen ions released through chelation:



and



(H_4Y represents ethylenediaminetetraacetic acid, M symbolizes any rare earth metal, and X designates an anion). The liberated protons were titrated with standard base using the Oscillometer to establish the end-points. All of the rare earths yielded

curves in which the amount of hydrogen ions released increased with increasing ratios of metal to addendum until 1 to 1 ratios were attained.

The experimental procedure can be illustrated by the typical case of lanthanum. One hundred milliliters of 1/3032M ethylenediaminetetraacetic acid were placed in the titration cell of the Oscillometer. Standard lanthanum nitrate was then added in increments selected to give definite metal to addendum ratios. The mixtures were stirred and the released protons were titrated with 1/90.9M sodium hydroxide. The resulting high frequency titration curves are illustrated in Fig. 1.

As shown in Fig. 1, the titration curve for the addendum alone gave an inflection point at two mole equivalents of base. With the addition of lanthanum the inflection point shifted progressively until at a 1 to 1 ratio, 4 mole equivalents of base were required. Up to this ratio, the end-points appeared as sharp reversals in the titration curves. Beyond this ratio there was no shift in the point of inflection and a pronounced alteration occurred in the shape of the curve. Excess lanthanum, beyond a 1 to 1 ratio, prevented the usual reversal of the titration curves and this may be interpreted

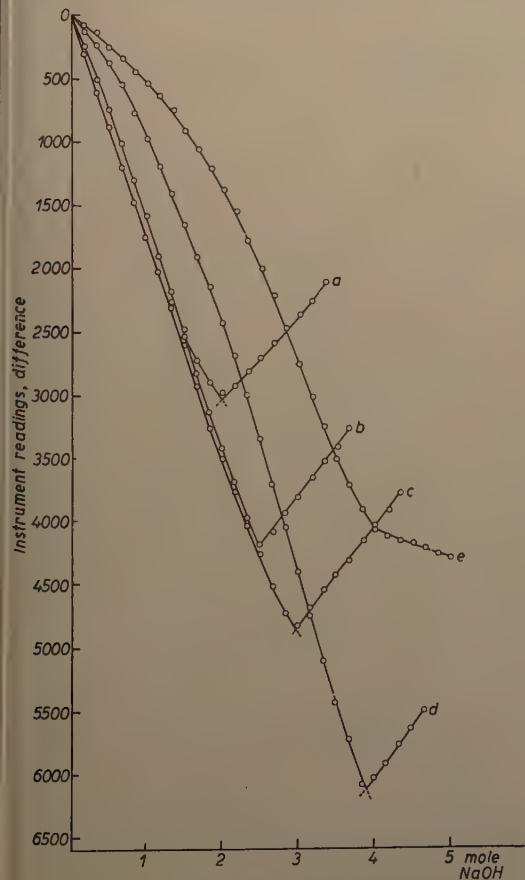


Fig. 1. Sodium hydroxide titrations of lanthanum nitrate and EDTA.

- (a) Addendum only
- (b) 1: 4 (La : addendum)
- (c) 1: 2 (La : addendum)
- (d) 1: 1 (La : addendum)
- (e) 2: 1 (La : addendum)

as indicating direct reaction between sodium hydroxide and uncomplexed (excess) metal.

The position of the inflection point is determined by the amount of metal present when excess complexer is present. This stoichiometric relationship lends itself to the quantitative estimation of lanthanum and the other rare earths.

A second approach employed for determining reacting ratios was to study simple, direct reactions between the rare earths and ethylenediaminetetraacetic acid. When a solution of a rare earth metal was added to a solution of the complexing addendum continuous complexation takes place. The course of the reaction can be followed by means of the Oscillometer and when an excess of metal ion is attained, a distinctive response is shown by the instrument. Lanthanum can again be used to illustrate the studies made of the various rare earth metals.

One hundred milliliters of $1/3000M$ ethylenediaminetetraacetic acid were placed in the large cell of the Oscillometer and titrated with $1/150M$ lanthanum nitrate.

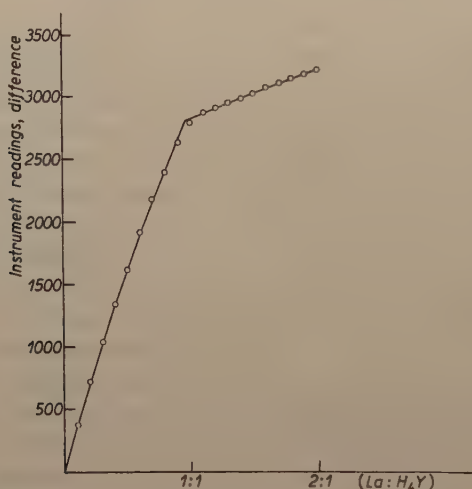


Fig. 2. Titration of $1/3000M$ EDTA with $1/150M$ lanthanum nitrate.

The titrations were made at the pH of the free acid (2.8–3.0), and at pH 10. The latter value was obtained by adjustment with $1/10M$ sodium hydroxide. The results of typical titrations are shown in Figs. 2 and 3.

The curve in Fig. 2 shows an increase in instrument reading until an end-point is obtained at reactant ratios of 1 to 1. The instrument response results from the release of protons during complexation. Beyond the end-point excess metal salt adds gradually to the Oscillometer response but the effect is much less than that given by liberated protons. The curve gives clear indication of 1 to 1 reaction ratios.

The curve shown in Fig. 3 represents a typical titration made at pH 10. In this case there is a slow decrease in instrument response until an end-point is reached at equal molar concentration of reactants. Up to this end-point the hydrogen ions being released in the reaction are removed due to the rather high alkalinity of the test medium. Beyond the end-point the titration curve drops sharply: this is probably

due to the precipitation of the metal hydroxide. The reversal point shown at approximately 1.5 mole of titrant marks the end-point of hydrolysis and the upward break of the curve represents the simple loading effect of added electrolyte.

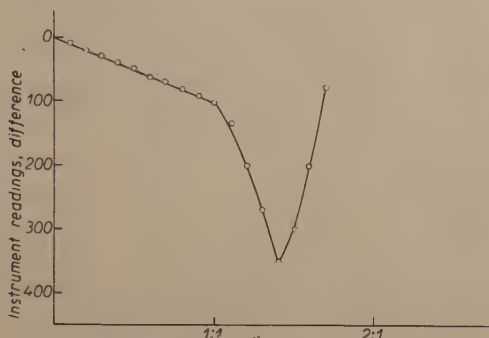


Fig. 3. Titrations of $1/1000M$ sodium EDTA with $1/50M$ lanthanum nitrate at pH 10.

Quantitative determination of rare earth metals

As mentioned in discussing the determination of reacting ratios, the hydrogen ions released through chelation of the rare earth metals and ethylenediaminetetraacetic acid are quantitatively related to the amount of metal present provided excess complexer is used. It is well known that this type of reaction can be used quantitatively by the simple expedient of titrating liberated protons with standard base. The Oscillometer can be recommended for use in such titrations.

A second quantitative technic is based on the direct titration of the rare earth metals with standard disodium ethylenediaminetetraacetate. It is to be recommended because of its simplicity. In the proposed method, 100 ml of test solution should be placed in the titration cell of the Oscillometer and titrated with the standard versenate. The titrant should preferably be standardized against pure salts of the metal to be determined. An alternate procedure is to add sodium acetate-acetic acid buffer (pH 5.3) before the titration. One ml of $1/5M$ buffer solution is sufficient for use with solutions of rare earths that are $1/3000M$ or less in strength. The use of the buffered solutions provides more distinct end-points as may be seen from Figs. 4 and 5.

The curves shown in Figs. 4 and 5 serve to illustrate the results obtained with all of the rare earths. The curves in Fig. 4 show that in unbuffered solutions an increase in instrument readings occurs up to the end-point. This effect is due to the liberation of hydrogen ions during the reaction. The characteristic curves shown in Fig. 5 indicate that the net ionic strength of the metal solution is reduced through complexation with the ethylenediaminetetraacetate. The buffer present removes the liberated protons so there is a sharp decrease in Oscillometer response as titrations progress. At the end-point an abrupt reversal occurs and further additions of titrant result in a pronounced load on the titrimeter. Continued additions of excess sodium ethylenediaminetetraacetate produce a steeply ascending curve.

Titrations in buffered solutions are quite accurate and small increments of titrant can be clearly indicated. Table I summarizes the results obtained in typical titrations conducted in buffered solutions. In all titrations, with the exception of gadolinium, errors ran under 0.5%. In the determination of gadolinium the errors were found

to run over 1% but this might be associated with the impurities which were known to be present in the gadolinium salts available.

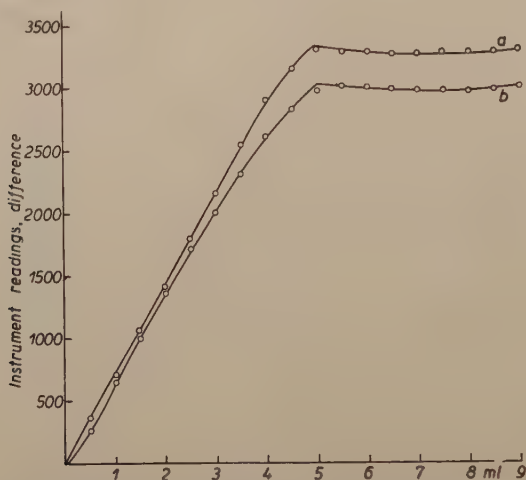


Fig. 4. Titrations of gadolinium bromate and cerous nitrate with disodium EDTA
 (a) Titration of $1/3012M$ gadolinium bromate with $1/150M$ disodium EDTA.
 (b) Titration of $1/3005M$ cerous nitrate with $1/150M$ disodium EDTA.

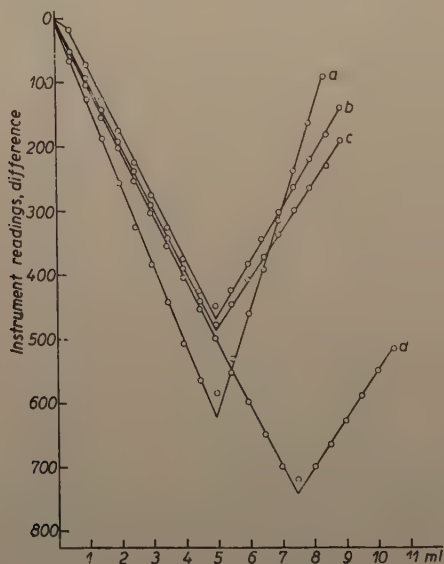


Fig. 5. Titration of cerous, praseodymium and neodymium nitrates with disodium EDTA in acetic acid sodium acetate buffer (pH 5.3).
 (a) Titration of $1/3005M$ cerous nitrate with $1/150M$ disodium EDTA.
 (b) Titration of $1/3010M$ praseodymium nitrate with $1/150M$ disodium EDTA in the presence of 8.71 mg barium nitrate.
 (c) Titration of $1/5998M$ neodymium nitrate with $1/300M$ disodium EDTA.
 (d) Titration of $1/4026M$ praseodymium nitrate with $1/300M$ disodium EDTA.

TABLE I

TYPICAL RESULTS OF DIRECT TITRATIONS IN BUFFERED SOLUTIONS

Rare earth taken (mg)	Molarity of titrant	Rare earth found (mg)	Error (%)
4.663 Ce ⁺³	1/150	4.680	0.36
4.663 Ce ⁺³	1/150	4.680	0.36
4.796 Nd	1/150	4.816	0.42
4.796 Nd	1/150	4.816	0.42
2.405 Nd	1/300	2.393	0.50

TABLE II

EFFECT OF ADDED ELECTROLYTES

Rare earth taken (mg)	Salt added (mg)	Rare earth found (mg)	Error %
4.663 Ce ⁺³	8.71 Ba(NO ₃) ₂	4.615	1.29
4.796 Nd	5.66 AgNO ₃	4.765	0.65
4.796 Nd	3.70 KCl	4.776	0.42

Interferences

Oxalates must be absent but chloride, iodide, bromide, thiocyanate, bromate, persulfate and chromate can be tolerated in small amounts. Of the cations only the alkali metals, ammonium, barium, strontium, silver, and thallium(I), are without serious effect. Excess salts, regardless of their nature, must be avoided because of the "loading" effect they exert on the high frequency titrimeter. The higher the salt concentration the less sensitive is the instrument. For solutions of rare earths in the range of 1/3000M "indifferent" electrolytes should not total over 1/2000M. Table II gives some results of titrations made in the presence of diverse salts.

DISCUSSION

Ethylenediaminetetraacetic acid reacts with rare earth metals at a 1 to 1 ratio. This reaction ratio has been confirmed by high frequency titrations over the pH range of 2.8 to 10, indicating that the rare earths form stable complexes over a wide range of acidities. In this regard, the rare earth metals differ from thorium.

Quantitative titrations of rare earth metals can be made using the high frequency titrimeter for following the course of the titrations. Direct titrations with disodium ethylenediaminetetraacetate and acetic acid-sodium acetate buffered solutions give the best results.

SUMMARY

High frequency titrations have been utilized in studying the chelation of rare earth metals with ethylenediaminetetraacetic acid. The use of high frequency titrations for the determination of rare earth metals has also been studied. A procedure is proposed based on direct titrations with disodium ethylenediaminetetraacetate in buffered solutions. Excellent end-points are obtained and the method is accurate in the absence of other metals that might react with the titrant.

RÉSUMÉ

Des titrations à haute fréquence ont été utilisées pour l'étude de la formation des chélates des métaux des terres rares avec l'acide éthylènediaminotétracétique. Ces titrations à haute fréquence ont également été étudiées en vue de leur application au dosage des métaux des terres rares. Une méthode est proposée; elle est basée sur la titration directe au moyen de l'éthylènediaminotétracétate disodique, en solutions tampons. Des points finals excellents ont été obtenus; la méthode est précise, en l'absence de métaux pouvant réagir avec le réactif.

ZUSAMMENFASSUNG

Hochfrequenztitrationen wurden zur Untersuchung von Metallchelaten der seltenen Erden mit der Äthylendiaminotetraessigsäure angewandt. Die Verwendung der Hochfrequenztitrationen für die Bestimmung der Metalle der seltenen Erden wurde gleichfalls untersucht. Es wird eine Methode vorgeschlagen, welche auf der direkten Titration mit Hilfe von Dinatriumäthylendiaminoacetat, in Pufferlösungen, basiert. Es wurden hervorragende Endpunkte erhalten. Die Methode ist präzise, falls keine Metalle vorhanden sind, die mit dem Reagenz reagieren können.

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INVERSE POLAROGRAPHY WITH STATIONARY AMALGAM ANODES

I. BASIC PRINCIPLES AND TECHNIQUE

by

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INTRODUCTION

A recent comprehensive investigation¹ of the anodic dissolution of stationary amalgam anodes has shown that the rate-determining factor is the diffusion of the metal in mercury up to the amalgam/electrolyte interface. When the potential of such an amalgam electrode is made progressively less negative, the metal begins to ionize and dissolve close to its reversible potential and the current rises to a limiting value which cannot be exceeded until some new dissolution process sets in. The limiting current density is very steady and reproducible, it is independent of the dissolution medium, it is only very slightly dependent upon temperature, and it is simply related to the concentration of the amalgam. Furthermore the limiting current is not complicated by the presence of any residual or migration currents, and its actual value can be made large by increasing the area of the amalgam anode. It is at once apparent that such metal diffusion currents may have important analytical applications, and in the present work an attempt has been made to utilize them for the detection, separation and estimation of the heavy metals which are soluble in mercury. The proposed method involves two main operations:

- (1) The metal ions present in an aqueous solution are electrolytically deposited in a mercury cathode. In this way they can be separated completely from acid radicals and organic material, and owing to the "gathering" power of the mercury cathode the metal ions from a large volume of very dilute solution can be collected.
- (2) The amalgam electrode formed in (1) is then washed and combined with a suitable reference electrode in an inert aqueous dissolution medium and the cell thus formed is allowed to supply current against an opposing voltage set up on a potentiometer. By decreasing the potentiometer voltage in stages and reading the current from a microammeter a discharge curve can readily be constructed in which each metal gives rise to a sharply defined wave which serves both to characterize it and to indicate its concentration in the amalgam.

CONDITIONS FOR QUANTITATIVE DEPOSITION OF METAL IONS

The rate at which metal ions can be discharged from an aqueous solution into a stationary mercury cathode is governed by the rate of convective diffusion of the ions in the aqueous medium to the electrode surface. If the ions are discharged in electrolysis at the limiting rate, then straightforward application of diffusion layer theory leads to the relation

$$C = C_0 \cdot e^{-\frac{ADt}{Vs}} \quad (1)$$

where C_0 is the initial concentration of the ions in g ion/ml, and C is the concentration after deposition for t seconds from V ml of solution into a cathode of area A sq.cm, D being the diffusion coefficient ($\text{cm}^2 \text{sec}^{-1}$) of the metallic ions and s the thickness of the diffusion layer in cm. This relation can be written as

$$t = \frac{2.303}{AD} Vs \log \frac{C_0}{C} \quad (2)$$

which predicts that the time required for the deposition of a given fraction of the metallic ions present is

- (i) independent of the initial concentration;
- (ii) directly proportional to the electrolyte volume;
- (iii) inversely proportional to the area of the cathode.

In terms of current, this equation becomes

$$t = \frac{2.303}{AD} Vs \log \frac{I_0}{I} \quad (3)$$

where I_0 is the initial limiting current and I that after time t .

Equation (3) was verified by LINGANE² for deposition of metallic ions from stirred solutions under conditions such that s is constant. In unstirred solutions the position is rather more complicated since the thickness of the diffusion layer tends to change slightly with variation of concentration, but a very full investigation has been made in the present work using thallium as test metal and depositing it under controlled potential conditions. The results show that provided allowance is made for variations in s (which can be done by using data from current/potential curves) equations (2) and (3) hold quite accurately and the predictions made have been verified.

To make a further test of the time-concentration equation (2) under less idealized conditions, a series of experiments was conducted in which the current was fixed at an arbitrary high value in excess of the limiting current for metal deposition so that hydrogen was freely and continuously evolved at the mercury cathode. Under these conditions stirring by hydrogen bubbles was found very greatly to increase the rate of metal deposition; the effect was considerably greater than that ordinarily produced by mechanical agitation of the solution. The gas stirring increased with rise of current density of hydrogen evolution but appeared to approach a constant maximum value when hydrogen was being evolved at current densities greater than 0.1 A/sq.cm. Under such conditions of constant gas stirring, equation (2) appeared to hold satisfactorily. The corresponding limiting thickness of diffusion

layer s was *ca.* 0.0004 cm at 20° C as compared with values of 0.01-0.03 cm for unstirred solutions. Using the value $s = 0.0004$ cm and taking $D \approx 10^{-5}$, equation (2) may be written

$$t \text{ (min)} \approx 1.5 \frac{V}{A} \log \frac{C_0}{C} \quad (4)$$

Thus for 1 ml of solution electrolysed with a 1 sq.cm mercury cathode under conditions of vigorous hydrogen evolution the time taken for a tenfold change in concentration of the metallic ion which is deposited should be approximately 1.5 min and more than 99.9% of the metallic ion should be removed from solution in a 5 min electrolysis.

This result was used as a guide in selecting conditions for satisfactory quantitative deposition of metallic ions. It was decided in general to use 1 ml of solution rendered highly conducting by addition of sulphuric or nitric acid and to electrolyse with a 1 sq.cm mercury cathode at 0.1 A current for 10 min. Numerous tests showed that under these conditions satisfactory quantitative deposition of heavy metallic ions at any initial concentration not greater than 0.1M could readily be achieved.

APPARATUS AND TECHNIQUE

The general apparatus and circuit arrangement adopted is shown in Fig. 1. 1 ml of mercury, measured from a small burette, is taken in a glass cup electrode (cross sectional area *ca.* 1 sq. cm) provided with sealed-in platinum contact and 1 ml of the acidified solution for analysis is pipetted on to it. A small platinum rod anode is introduced into the solution which is electrolysed at 0.1 A for 10 min. The anode is then withdrawn, the electrolyte washed out with water, the amalgam stirred with a small glass ring stirrer, and the cup is then ready for use as an amalgam anode. For this purpose it is necessary to combine it with a large unpolarizable reference electrode of low resistance in a suitable dissolution medium. It has been found that a very suitable reference electrode consists of mercury in contact with excess mercurous sulphate in saturated potassium sulphate solution. This may be conveniently set up and used repeatedly by placing the mixture in the lower part of a sintered glass funnel; a fresh portion of dissolution medium is then placed above the sintered glass diaphragm for each experiment and the cup anode immersed directly in it. Saturated potassium sulphate has been most frequently used as dissolution medium, although potassium nitrate has been employed in some cases where the metallic sulphate formed by dissolution was sparingly soluble. The measured potential of the reference electrode on the hydrogen scale at 18° C is + 0.66 V, and using the arrangement described with a funnel of about 5 cm diameter and 7 cm deep the internal resistance can be kept below 30 Ω .

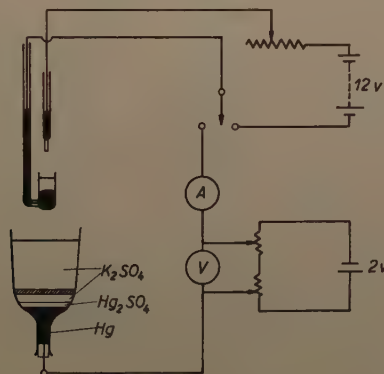


Fig. 1. Apparatus and circuit.

The voltage between the amalgam and reference electrode is opposed by a small potentiometer-voltmeter unit. This is initially set so that the potential of the amalgam is strongly negative and no current flows. The potentiometer voltage is then reduced in stages and the current passing at each setting of the potentiometer is read off from the milliammeter A which has ranges of 100 μ A, 1 mA, and 10 mA severally. When a metal in the amalgam first begins to dissolve there is usually a surge of current, but this falls rapidly to a steady value as the diffusion layer is set up in the mercury surface and no difficulty is experienced in obtaining a steady current reading. Very occasionally maxima similar to those observed in polarography are apparent at the beginning of the limiting current stage but the presence of 0.01% gelatin in the dissolution medium suppresses them and improves the steadiness of the limiting currents, and this addition has generally been made. If the current is held at its limiting value for several minutes then it may fall owing to diminution in the concentration of the amalgam, but no difficulty is normally experienced in adjusting the period of observations so as to avoid errors due to this effect.

RESULTS

Typical curves

In Fig. 2 are shown typical curves for a number of common metals at different concentrations. The amount of metal indicated in each case was that present in 1 ml of the original aqueous solution; this amount was transferred to the 1 ml of mercury in the preliminary electrolysis and the curve is that for the anodic dissolution of the amalgam formed. It may be noted that each curve rises sharply from the potential axis and the initial dissolution potential seems to characterize the metal present. The current rises steeply to the limiting value and then generally remains very steady until the potential of the amalgam approaches that of the reference electrode when mercury passes into solution; the potentiometer voltage is then zero and the amalgam potential is + 0.66 V on the hydrogen scale. Using a milliammeter with the ranges specified (100 μ A to 10 mA) limiting currents corresponding to 10^{-6} to 10^{-4} eqt. of most metals could be accurately measured.

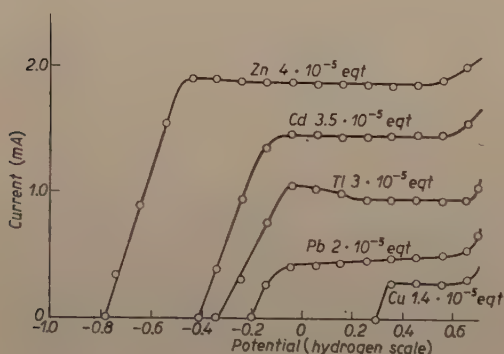


Fig. 2. Typical amalgam dissolution curves.

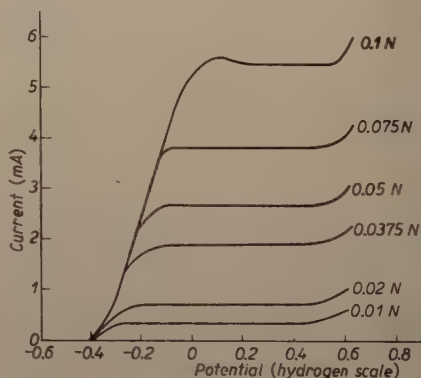


Fig. 3. Current-potential curves at different cadmium ion concentrations.

Reproducibility and concentration dependence of limiting current

In Table I is shown a set of results obtained for the dissolution of cadmium in amounts varying from 10^{-4} to 10^{-6} eqt., the concentration of the initial aqueous solution which contained 0.1N- H_2SO_4 being varied from 0.1 to 0.001N with respect to cadmium sulphate; some of the corresponding curves are plotted in Fig. 3.

It is at once apparent that it is the initial dissolution potential rather than the half wave potential which characterizes the metal. The relation of limiting current to concentration is shown in Fig. 4. Over any small range of concentration the relation is approximately linear, but over wide ranges of concentration it is more accurately expressed as $I = k C^{1.25}$ and this relation has been shown to apply fairly generally¹. To check the reproducibility of the starting potential and limiting current value, seven separate experiments were carried out analysing 1 ml portions of 0.01N- CdSO_4 in 0.1N- H_2SO_4 . The results are summarized in Table II and it can be seen that both the initial dissolution potential and the limiting current are remarkably steady.

TABLE I
ANODIC DISSOLUTION OF CADMIUM

Concn. CdSO_4 in aq. soln.	Amt. of metal transferred	Initial diss. potl.	Half wave potl.	Limiting current
0.1N	$100 \cdot 10^{-6} \text{eqt.}$	-0.41 V	-0.19 V	5.50 mA
0.075	75	-0.41	-0.25	3.80
0.05	50	-0.41	-0.28	2.70
0.0375	37.5	-0.41	-0.33	1.90
0.02	20	-0.41	-0.31	0.73
0.01	10	-0.41	-0.34	0.37
0.005	5	-0.41	-0.35	0.175
0.002	2	-0.39	-0.33	0.057
0.001	1	-0.39	-0.32	0.017

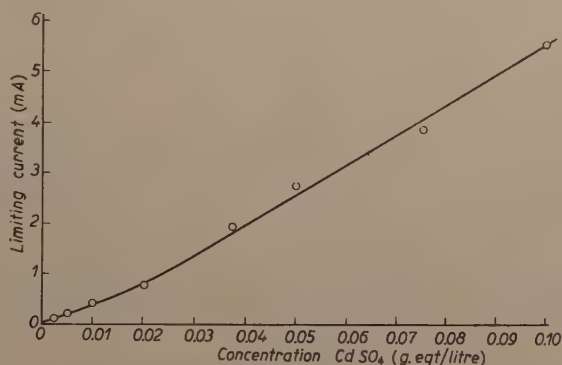


Fig. 4. Dependence of limiting dissolution currents on initial cadmium ion concentration.

TABLE II
REPRODUCIBILITY IN ANODIC DISSOLUTION OF CADMIUM (10^{-5} eqt.)

No. of expt.	Initial diss. potl.	Limiting current
1	-0.41 V	0.37 mA
2	-0.41	0.365
3	-0.41	0.37
4	-0.41	0.37
5	-0.41	0.37
6	-0.41	0.385
7	-0.41	0.365

To see what influence the period of initial electrolysis at 0.1 A had, separate experiments were carried out using 1 ml of 0.01N- CdSO_4 in which periods of 10, 5, 4, and 3 min electrolysis were employed. Only in the last case did the limiting current show any falling off confirming that the usual period of 10 min is more than adequate.

To find what effect temperature variation would have upon the limiting current of dissolution experiments were carried out at temperatures ranging from 0 to 54° C and the results are summarized in Table III.

TABLE III
INFLUENCE OF TEMPERATURE ON ANODIC DISSOLUTION OF CADMIUM (10^{-5} eqt.)

Temperature °C	0	17	34	54
Limiting current mA	0.36	0.37	0.43	0.47

It is apparent that any normal variation of room temperature will have very little influence on the magnitude of the limiting current observed.

It might be expected that any factor influencing the area of the interface between the amalgam anode and the dissolution medium would change the limiting current, and some irreproducibility in the value might arise from variable penetration of the electrolyte between the mercury and the sides of the glass cup. That this effect does exist was shown by introducing various amounts of glass wool into the mercury surface when the limiting current was appreciably increased. Under ordinary conditions, however, the effective anodic area seems to remain very reasonably constant in different experiments. Addition of capillary active substances such as teepol to the dissolution medium at concentrations of 0.01 and 0.1% did not affect the magnitude of the limiting current substantially although the flatness of the wave deteriorated somewhat, and the presence of such substances should generally be avoided.

Collection of metallic ions from very dilute solutions

By increasing the time of the preliminary electrolysis a larger volume of aqueous sample may be estimated. Thus metallic ions in extremely dilute solutions can be gathered into the mercury electrode which will subsequently give a substantial anodic limiting current. To demonstrate this, samples containing 10^{-5} eqt. of cadmium in 1, 10, 100, and 1000 ml of solution severally were analysed by the present technique and the results are given in Table IV. For the larger volumes of solution the cup electrode was placed at the bottom of the solution contained in a tall beaker and the platinum electrode near the top; the deposition current was increased to 0.2 A to produce bulk stirring by the gas evolution. Taking the essential period for quantitative deposition from 1 ml of solution to be 5 min, the time was increased proportionately for the larger volumes of solution.

TABLE IV
ESTIMATION OF CADMIUM FROM VARIOUS SAMPLES (10^{-5} eqt.)

Vol.	Sample	Concn.	Time of electrolysis	Initial diss. potl.	Limiting current
1 ml	10^{-2} N-CdSO ₄		5 min	-0.41 V	0.37 mA
10	10^{-3}		50	-0.41	0.37
100	10^{-4}		500	-0.41	0.37
1000	10^{-5}		5000	-0.41	0.37

It is seen that the cadmium has been quantitatively recovered from all solutions and gives the same limiting dissolution current. In a further of experiments using 10^{-6} eqt. cadmium the metal was quantitatively recovered from 1000 ml of 10^{-6} N-CdSO₄ in 0.1N-H₂SO₄ by electrolysis for ca. 5 days to give the usual anodic dissolution current of 0.017 mA.

Mixed amalgams

The conclusions drawn from the results which have been described in detail for cadmium apply equally well to manganese, zinc, lead, thallium, and copper all of which give good anodic dissolution waves. Under the deposition conditions specified from an acid medium the alkali and alkaline earth metals do not form stable amalgams and are not detected in the anodic dissolution; likewise metals such as nickel, iron and chromium which are practically insoluble in mercury fail to give anodic waves.

When mixtures of metallic ions are used the characteristic anodic wave of each metal shows up in the dissolution curve. Thus in Fig. 5 is shown the curve for a mixture of 10^{-5} eqt. each of zinc and cadmium, while in Fig. 6 the graph corresponding to $2.5 \cdot 10^{-5}$ eqt. each of zinc and thallium is given. The limiting currents to be expected from the behaviour of the metals separately

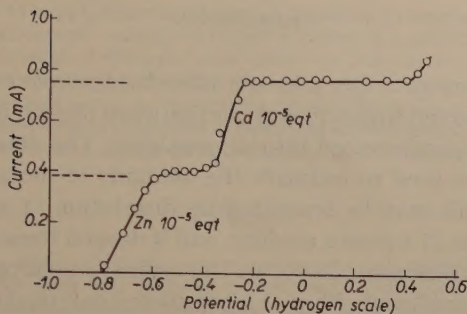


Fig. 5. Dissolution curve for mixture of zinc and cadmium.

are indicated by the dotted lines to the left of the diagrams. It is noteworthy that the first metal to dissolve from the amalgam gives its expected limiting current quite accurately and this has been generally confirmed. Subsequent limiting currents, however, sometimes tend to be higher than those expected from the behaviour of the metals singly. This effect, which has also been noted with dropping amalgam anodes³, appears to arise by a simple electrochemical displacement reaction. When a second metal such as thallium enters the solution while the amalgam still contains a more reactive metal such as zinc, the displacement reaction $2\text{Tl}^+ + \text{Zn} = 2\text{Tl} + \text{Zn}^{+2}$ may occur raising the surface concentration of thallium and exalting its limiting current. The effect can be minimized by avoiding any accumulation of dissolved metal ions near the amalgam surface, but it is difficult to eliminate it entirely, and it constitutes a limitation on the inverse polarographic method of analysis as applied to mixtures of metallic ions.

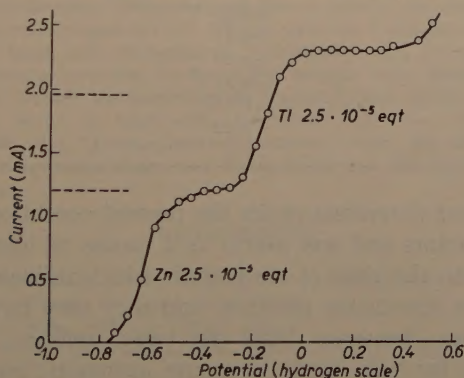


Fig. 6. Dissolution curve for mixture of zinc and thallium.

Calibration

For the estimation of any particular metal it is most satisfactory to obtain a series of limiting anodic dissolution currents with known amounts of the metal present using the cup electrode which is to be subsequently employed. With suitable calibration values obtained in this way an unknown amount of a single metal greater than *ca.* 10^{-6} eqt. can then be determined with an accuracy of about $\pm 1\%$. No attempt has so far been made to push the method to its extreme limit, although it is obvious that by increasing the sensitivity of the current measuring device much smaller quantities of metal could be estimated.

By utilizing coulometric aspects of the anodic dissolution process the necessity of calibration can be avoided although with some loss of accuracy and convenience. Thus if the potentiometer voltage is fixed at such a value that one metal only can go into solution, a graph of limiting current against time can be constructed for the duration of the dissolution process. Graphical integration then gives the quantity of electricity corresponding to the metal which has dissolved. This method is rather time consuming (1-2 hours) and the results tend to be low (within *ca.* -5%). The period may be reduced by various devices such as measuring the quantity of electricity which passes while a known fraction of the metal dissolves as indicated by the limiting current, but again the accuracy attained is not better than about -5% .

DISCUSSION

The present technique provides a means whereby a number of heavy metals may be quantitatively extracted from aqueous solution when present in minute amounts and at high dilutions and concentrated into an amalgam. The anodic dissolution of the amalgam may then be used to estimate the amounts of metal present directly, or alternatively the metals may be separated by dissolution at appropriate potentials into successive portions of aqueous medium and if desired these can then be analysed by other means, *e.g.* colorimetrically or by the ordinary polarographic method. Thus the technique can be employed either as a complete analytical method or as a useful preliminary operation of concentrating and separating metallic ions prior to analysis by other means.

In the anodic dissolution of metallic amalgams by the present method the initial dissolution potentials are sharply defined and seem to be fairly constant under different experimental conditions. The values are usually quite close to the standard potentials of the metals, as the following figures show, and they serve as an adequate means of characterization.

<i>Metal</i>	<i>Initial dissolution potential</i>	<i>Standard potential</i>
Cu	+0.30 V	+0.34 V
Pb	-0.15	-0.12
Tl	-0.26	-0.33
Cd	-0.41	-0.40
Zn	-0.78	-0.76
Mn	-1.12	-1.05

The anodic half-wave potentials under the present condition are more dependent upon experimental factors and less useful as a means of identification. Thus they may vary according to the time of electrolysis which influences the concentration of metallic ions in the dissolution medium, and they may be markedly displaced if the circuit resistance becomes high for any reason.

No attempt has so far been made to secure automatic recording of the anodic dissolution waves since one advantage of the method as described is the very simple apparatus which is required. There would appear, however, to be no great difficulty in adapting the ordinary type of recording polarograph for use with stationary amalgam anodes, and this is at present under investigation. Previous attempts to use amalgam anodes for analytical purposes have generally employed dropping amalgam electrodes and have not led to any conspicuously successful application. In the present work it is the particular features of a stationary mercury pool electrode in first serving as a cathode for the collection of metallic ions and subsequently as a large anode for metal dissolution at substantial currents which permit of useful analytical employment.

SUMMARY

A new method of electrochemical analysis has been devised in which the metallic ions present in an electrolyte are discharged into a mercury cathode. The amalgam electrode so formed is then combined with a standard reference electrode in a suitable dissolution medium and the cell

thus produced is allowed to supply current against an opposing voltage set up on a potentiometer. By decreasing the potentiometer voltage in stages a curve of current against potential can be constructed for the dissolution of the amalgam anode; in this curve each metal gives rise to a characteristic wave from the height of which the amount of metal originally present can be derived. Although the method is not so universally applicable as the conventional polarographic technique with the dropping mercury cathode, it possesses advantages in sensitivity and simplicity in suitable cases and may form a useful complementary method of analysis.

RÉSUMÉ

Un nouvelle méthode électrochimique est proposée; les ions métalliques présents dans un électrolyte sont déchargés dans une cathode de mercure. L'électrode amalgamée ainsi formée est ensuite reliée à une électrode étalon de référence dans un milieu convenable; l'on fait fournir du courant à la pile ainsi obtenue en sens opposé à une tension appliquée à un potentiomètre. En diminuant le voltage du potentiomètre graduellement, une courbe de courant en fonction du potentiel peut être construite, pour la dissolution de l'anode amalgamée. Dans cette courbe, chaque métal donne une onde caractéristique, dont la hauteur permet de déterminer la teneur en métal présent. Bien que cette méthode ne soit pas aussi généralement applicable, que la technique polarographique usuelle avec la cathode à gouttes de mercure, elle présente des avantages de sensibilité et de simplicité dans certains cas; elle peut constituer une méthode d'analyse complémentaire utile.

ZUSAMMENFASSUNG

Es wird eine neue elektrochemische Methode vorgeschlagen; die in einem Elektrolyt vorhandenen Metallionen werden an einer Quecksilberelektrode entladen. Die so gebildete Amalgam-elektrode wird darauf mit einer Vergleichselektrode in einem entsprechenden Medium verbunden. Man lässt dann das so entstandene Element einen Strom liefern, der einer auf ein Potentiometer angewandten Spannung entgegengesetzt ist. Wenn man die Voltspannung des Potentiometers stufenweise vermindert, kann eine Stromkurve in Funktion des Potentials für die Auflösung der Amalgamanode konstruiert werden. In dieser Kurve gibt jedes Metall eine charakteristische Welle, deren Höhe den Gehalt an ursprünglich vorhandenem Metall zu bestimmen erlaubt. Obwohl diese Methode nicht so allgemein anwendbar ist, wie die gewöhnliche polarographische Technik mit der Quecksilbertropfkathode, weist sie doch in gewissen Fällen Vorteile in Bezug auf Empfindlichkeit und Einfachheit auf. Sie kann eine nützliche Ergänzungsanalyse-methode sein.

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Analysis of Insecticides and Acaricides, by F. A. GUNTHER AND R. C. BLINN, Interscience Publishers, Inc., New York and London, 1955. viii + 696 pp., 71 fig.; price £ 5. 12.

The rapidly increasing use of insecticides, many of which are extremely toxic to human beings, has created a demand for the analysis of the insecticides themselves, and of the edible fruit or vegetables to which they have been applied. As far as the reviewer is aware, this is the first book which covers existing knowledge in this field, and it fulfils its purpose admirably. The authors have obviously drawn freely on their experience from 12 years of research activity in the analysis of insecticides and their residues on plants.

The book constitutes Vol. VI in a series of monographs on analytical chemistry and its applications, edited by B. L. CLARKE AND I. M. KOLTHOFF. It is divided into three sections: the first is a detailed discussion of the problems involved in securing quantitative data on insecticide residues on fruits and foliage, such as sampling considerations, sample processing, preanalysis or clean-up treatment, the analysis, interpretation of data, expression of results and health hazards (161 pages). Section 2 (8 pages) gives some general notes on the composition analysis of technical products. Section 3 has some 40 pages giving detailed general instructions for field sampling, measurement of samples, processing and clean-up procedures (for isolating the insecticide residues from interfering substances). These are followed by 450 pages giving in detail analytical procedures for some 90 individual insecticides and acaricides, together with a general section on determination of organic phosphorus. In general, methods are given both for composition analysis and residue analysis. The authors have drawn their methods from a wide field (almost entirely American), which includes manufacturers such as American Cyanamide, Dow Chemical, Geigy and Shell Development, and the State of California Dept. of Agriculture. All modern resources, such as infra-red spectroscopy and chromatography, are freely used. There are appendices giving detailed ultra-violet and infra-red spectra for a number of purified insecticides and acaricides and some possible accessory substances.

N. STRAFFORD (Manchester)

BUCHBESPRECHUNG

Qualitative chemische Analyse, von AUTHENRIETH-ROSENMUND, 4. völlig umgearbeitete Auflage von Prof. Dr. K. W. ROSENMUND, Verlag Th. Steinkopff, Dresden und Leipzig, 1955, viii und 152 S., 11 Abb.; brosch.: Schw. Fr. 9.30, geb.: Schw. Fr. 10.35.

Für die allgemeine Beliebtheit von AUTHENRIETH-ROSENMUNDS *Qualitative chemische Analyse* spricht der Umstand, dass bereits wieder eine Neuauflage und zwar die vierte notwendig geworden ist. Diese Neuauflage stellt eine wesentliche Erweiterung und auch Verbesserung dar. Besonders begrüßenswert ist, dass nunmehr auch moderne Analysenmethoden mehr als bisher Berücksichtigung fanden. So sind neben der bekannten Ammon-Sulfid-Fällung auch die Hydrolysen-trennung mittels Hexamethylentetrammin und dessen Vorteile beschrieben. Der I. Abschnitt bringt die für das analytische Arbeiten und für das Verständnis der Vorgänge notwendigen theoretischen Grundlagen: Ionenlehre, elektrolytische Dissoziation, Hydrolyse, chemisches Gleichgewicht, Löslichkeitsprodukt, Spannungsreihe, pH-Definition, Pufferlösungen, Komplexverbindungen, die zweckmässig in knapper Form gehalten sind, sodass eine Überlastung des Anfängers dadurch vermieden wird. Aus dem gleichen Grunde und um dem Anfänger die Übersicht zu erleichtern, sind die sogenannten selteneren Elemente (Rb, Cs, Au, Be, Ce, Ti, Zr, Th, V, Se, Te, Mo, W, U, Pt) am Schluss des Buches im IV. Abschnitt behandelt. Der Zweck, sowohl eine Anleitung für den Anfänger als auch eine Hilfe für den Anspruchsvolleren zu bieten, erscheint durch diese Einteilung in befriedigender Weise erreicht zu sein. Im II. Abschnitt sind die wichtigsten Nachweisreaktionen der Kationen (Na, K, Li, NH₄, Mg, Ca, Sr, Ba, Al, Cr, Fe, Zn, Mn, Ni, Co, Hg, Cu, Pb, Bi, Cd, As, Sb, Sn, Ag, Tl) und Anionen in der bekannten klassischen Gruppeneinteilung beschrieben. Der III. Abschnitt ist der für den Anfänger besonders wichtigen Beschreibung des Analysenganges gewidmet: Vorproben, Analyse auf trockenem und nassem Wege, einschliesslich des in Tabellenform gebrachten Trennungsganges der Kationen und des Nachweises der Anionen. Im V. Abschnitt sind die in diesem Buch verwendeten organischen Nachweisreagenzien zusammengestellt. In diesem Zusammenhang ist es zu begrüßen, dass in der vorliegenden Auflage von den organischen Reagenzien vermehrter Gebrauch gemacht wird und auch die mikrochemischen Nachweismethoden eine stärkere Berücksichtigung finden. Auf jeden Fall kann dem Anfänger aber auch dem Fortgeschrittenen dieses Buch sehr empfohlen werden, da es einen sehr schönen Überblick über die gebräuchlichen qualitativen Methoden gibt.

G. GORBACH (Graz)